DERIVATIVES AND REACTIONS OF GROUP VB ORGANOMETALLOIDAL AND QUATERNARY COMPOUNDS

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SUMMARY

Derivatives and Reactions of Group VB Organometalloidal and Quaternary Compounds

The major part of this thesis is devoted to a description of the chemistry of metal halide (principally mercuric iodide) derivatives of Group VB quaternary 'onium halides and organometalloidal compounds. The other section contains a discussion of the reactions of some Group VB organometalloidal compounds with trifluoroiodomethane, and of the solvent properties of liquid trifluoroiodomethane.

The iodomercurate(II) complexes of the tetramethylammonium, tetramethylphosphonium, pyridinium, and triphenylmethylarsonium cations have been prepared. The infra-red spectra of tetramethylphosphonium iodide and its iodomercurate complexes have been measured in the region 500-2500 cm^{-1}, and the observed absorption bands have been tentatively assigned to vibrations associated with the tetramethylphosphonium cation.

It has been shown that quaternary iodomercurate(II) complexes decompose, when heated in aqueous suspension, to give either quaternary iodomercurate(II) complexes with a lower iodine:mercury ratio or mercuric iodide, and a quaternary iodide. The reactions form a stepwise pattern.

By means of ultra-violet spectroscopy it has been shown that the tri-iodomercurate ion is the predominant anionic iodomercurate species present in dilute solutions (ca. 10^{-4} M) of iodomercurate complexes of each stoichiometric class (viz., Q_2HgI_4, $QHgI_3$, $Q_2Hg_3I_8$, and QHg_2I_5 - where Q is a quaternary cation). Theoretical spectra of the undissociated tri-iodomercurate ion have been calculated, and an approximate equilibrium constant for the reaction, $HgI_2 + I^- \rightleftharpoons HgI_3^-$, in methanol at 25°, has been found. The conductivities of a number of iodomercurate complexes in acetone have also been measured.

It has also been shown that iodomercurate complexes react with triphenylphosphine in acetone or ethanol solution with the formation of an iodo(triphenylphosphine)mercury(II) complex, and either a quaternary iodomercurate(II) complex with a higher iodine:mercury ratio or a quaternary iodide. These reactions may be adapted as an analytical method for the determination of the mercuric iodide (or mercury) content of iodomercurate complexes.

The conversion of halo(triphenylphosphine)mercury(II) complexes to Group VB quaternary 'onium halomercurate(II) complexes by alkyl halides has been studied. Analogous reactions of halo(triphenylphosphine)cadmium(II) complexes have also been investigated. Quaternary bromo- and bromo-iodomercurate(II) complexes were found to undergo halogen exchange readily with alkyl iodides to give quaternary iodomercurate(II) complexes. However, quaternary tri-iodomercurates do not react readily with alkyl bromides.

The results of exploratory investigations of the reactions of triphenylphosphine, triphenylarsine, phenyldimethylamine, and phenyldimethylphosphine with trifluoroiodomethane are presented in the second part of the thesis. Qualitative solubilities of a number of compounds in trifluoroiodomethane have also been determined.

To the best of the author's knowledge this thesis contains no material which has been published by other persons or submitted for a degree in any University by the author or other persons, except where due reference is made in the text.

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INTRODUCTION

Organometallic and organometalloidal compounds are generally defined as having carbon-metal and carbon-metalloid bonds respectively.[1,2] Thus the compounds dimethylzinc and tetraethyl-lead would be classified as organometallic compounds, while triphenylarsine and diphenylgermanium dichloride would be organometalloidal compounds. Within Group VB it is desirable to extend the use of the term "organometalloidal" to include compounds such as triphenylphosphine and phenyldimethylamine containing direct bonding of carbon to the Group VB element, as there are similarities between the bonding and reaction chemistry of these compounds and their arsenic analogues which make it convenient to discuss and classify them together. It is in this extended sense that the term "organometalloidal" is used throughout this thesis.

The Group VB quaternary compounds to be considered are salts of Group VB quaternary 'onium cations, e.g., tetramethylphosphonium iodide. Strictly the term "quaternary" should only be used as an adjective, as in quaternary phosphonium, however it is commonly used to denote a Group VB quaternary 'onium cation,[3] both to avoid tedious repetition of the systematic name of a cation and also when a general account is being given of the properties of these ions and their salts. Thus tetramethylphosphonium iodide may be termed a quaternary iodide. This practice is followed throughout this thesis.

The derivatives of Group VB organometalloidal compounds to be discussed are those formed by trivalent organometalloidal compounds with mercuric and cadmium halides. Attention is mainly confined to those formed by triphenylphosphine with these metal halides, e.g., diiodobis(triphenylphosphine)mercury(II), $[Ph_3P]_2HgI_2$.*

The derivatives of Group VB quaternary compounds to be considered are mercuric halide (principally mercuric iodide) derivatives of quaternary halides, e.g., triphenylmethylarsonium tri-iodomercurate(II), $[Ph_3AsMe][HgI_3]$.

The thesis is divided into two parts. In Section A (Chapters 1–5) the preparations and properties of quaternary halomercurate(II) and halo(triphenylphosphine)mercury(II) and -cadmium(II) complexes are discussed. Chapter 1 is devoted to a review of the known properties of these and related compounds. In the subsequent chapters the original work is described. Chapters 2 and 3 contain a discussion of the preparation and properties of quaternary iodomercurate(II) complexes, in Chapter 4 the reactions of halo(triphenylphosphine)mercury(II) and -cadmium(II) complexes and of quaternary halomercurate(II) complexes with alkyl halides are described, while the detailed experimental results are given in Chapter 5.

The original work to be described in Section B is an exploratory study of the reactions of some Group VB organometalloidal compounds with trifluoroiodomethane, and a qualitative investigation of solubilities in liquid trifluoroiodomethane. Chapter 6 contains a brief review of the reactions of Group VB organometalloidal compounds with haloalkanes. The original results are discussed in Chapter 7,

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* Abbreviations for organic radicals are used continually, and are those approved by the Chemical Society of London.[4]

and Chapter 8 contains the experimental section. The reactions studied have proved complex, and their investigation is at this stage incomplete, and further work is intended.

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SECTION A

CHAPTERS 1 - 5

DERIVATIVES OF GROUP VB ORGANOMETALLOIDAL AND QUATERNARY COMPOUNDS

CHAPTER 1

Review of the Properties of Halomercurate(II) Complexes and Halo (tertiary phosphine and arsine)mercury(II) and -cadmium(II) Complexes

Mercuric halide and cadmium halide derivatives have been used extensively for the characterization of Group VB quaternary halides and organometalloidal compounds. As will be shown in the following review, there are significant gaps in the known chemistry of these compounds, and attempts to provide a more detailed understanding of their properties form the major part of this thesis.

A. The Chemistry of Halomercurate(II) Complexes.

The review contains a discussion of most known types of halomercurate(II) complexes, and is not restricted to those formed by Group VB quaternary cations. Iodomercurate complexes are considered in more detail than bromo-, chloro-, and fluoromercurate complexes.

Fluoromercurates are the least stable halomercurate complexes.[1] Complex fluoromercurate anions have not been detected in solution.[2] Recently however a number of crystalline quaternary ammonium tetrafluoromercurate(II) complexes have been isolated.[3]

It is convenient to divide the chemistry of halomercurate(II) complexes into two sections, the properties of the crystalline complexes and the properties of the complexes in solution.

Properties of the Crystalline Complexes.

Stoichiometries of the Crystalline Complexes.

The alkali metal halomercurate(II) complexes generally have the stoichiometries M_2HgX_4 and $MHgX_3$ (where M is an alkali metal, and

X is Cl, Br, or I) and may also contain water of crystallization. Detailed lists of compounds reported are given elsewhere.[4-8] The majority of the alkaline earth metal and heavy metal halomercurate(II) complexes have a mercury:halogen ratio of 1:4. The specific compounds prepared have been summarized by others.[5-8]

There are four stoichiometric classes of the quaternary iodomercurate(II) complexes, viz., tetraiodomercurates Q_2HgI_4, tri-iodomercurates $QHgI_3$, pentaiododimercurates QHg_2I_5, and octaiodotrimercurates $Q_2Hg_3I_8$ (where Q is a Group VB quaternary cation). Compounds of these four classes are also known for the analogous sulphonium iodomercurates. Quaternary and sulphonium chloro- and bromomercurate complexes generally have the stoichiometries Q_2HgX_4, and $QHgX_3$ (where Q is a Group VB quaternary cation or a sulphonium cation, and X is Cl or Br), but examples of other stoichiometries are known, e.g., $[Me_2NH_2][Hg_2Br_5]$ [9] and tris(dl-phenacylmethylethylsulphonium) heptachlorodimercurate(II).[10] Iodomercurate(II) complexes of the more common Group VB quaternary cations and the more common sulphonium cations are given in Table 1.1. There is some disagreement as to the number of complexes formed by various cations. Thus François[15] reported four pyridinium iodomercurates, but Lal Datta[12] obtained only the tetraiodomercurate complex using a similar preparative method. Earlier workers obviously confused tetraethylammonium tri-iodomercurate(II) and bis(tetraethylammonium) octaiodotrimercurate(II).[11,13] It has recently been shown that the compound m.p. 110° is the authentic tri-iodomercurate.[14] For many cations only the tri-iodomercurate complex has been reported, and it is likely that other complexes could be prepared. In Chapter 2 the

TABLE 1.1

Iodomercurate Complexes of the More Common Group VB Quaternary Cations

Cation	HgI_4 Complex		HgI_3 Complex		Hg_2I_5 Complex		Hg_3I_8 Complex	
	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.
Me_2NH_2			11	122°				
Me_3NH			11	136°				
Et_2NH_2			11	114°				
Et_3NH			11	77-78°				
Me_4N	12	not given	11	236°			12	not given
			13	>200°				
$MeEt_3N$			13	104°				
Et_4N	12	not given	13	110°			13	154°
			11	155°			12	not given
			14	110°				
Et_3Pr^nN			13	85°				
$MePr_3^nN$			13	123°				
$EtPr_3^nN$			13	135°				
Pr^n_4N			13	178°				
PyH	15	159°	15	151°	15	121°	15	101°
	12	not given	16	152-154°				
$PhMe_3N$			13	135°				
			17	137-138°				
$PhMe_2EtN$			13	95°				
			17	97.5°				
$PhMeEt_2N$			13	96°				
			17	98.5°				
$PhEt_3N$	13	144°	13	98°	17	113°		
Me_4P					18,19	172°		
Et_4P	19	202°			19	117°		
Me_4As			20	184°				
Et_3AsMe	21	253°	21	64°				
Et_4As	22	238°	22	117°				
			23	112°				
Pr_4^nAs			20	120°				
Pr_4^iAs			20	114°				

TABLE 1.1 (contd.)

Cation	HgI_4 Complex		HgI_3 Complex		Hg_2I_5 Complex		Hg_3I_8 Complex	
	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.
$PhMe_3As$			22	128°				
$PhMe_2EtAs$			24	135°				
$PhAsEt_3$			22	129°				
Ph_2AsMe_2			22	131°				
Ph_2AsEt_2			22	86°				
Et_4Sb							25	ca. 70°

Iodomercurate Complexes of the More Common Sulphonium Cations

Cation	HgI_4 Complex		HgI_3 Complex		Hg_2I_5 Complex		Hg_3I_8 Complex	
	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.	Ref.	m.p.
Me_3S	26	184°						
Me_2EtS	27	173°	27	85°				
$MeEt_2S$	27	150°	27	66-67°				
Et_3S	10	150-151°	10 28	112-113° 110°	10 28	121-122° 114-115°		
Me_2Pr^nS	27	95°	27	72-73°				
$MePr_2^nS$			27	106°				
$PhSEt_2$	10	114-115°	10	56-57°			10	65-66°

preparation and characterization of tetramethylammonium, tetramethylphosphonium, triphenylmethylarsonium, and pyridinium iodomercurates is described.

The Structure of Crystalline Halomercurate(II) Complexes.

The structures of the complexes $K_2HgCl_4.H_2O$ [29] and NH_4HgCl_3 [30] have been examined by X-ray diffraction. Crystals of the former complex do not contain $HgCl_4{}^{2-}$ ions, and it was suggested that the structure is based on $HgCl_6$ octahedra linked edge to edge, the chains of octahedra being held together by potassium ions and water molecules. Similarly it was considered that crystals of NH_4HgCl_3 do not contain $HgCl_3{}^-$ ions but are built from layers of $HgCl_6$ octahedra held together by ammonium ions. Since two mercury-chlorine bond distances are much smaller than the other four in this complex, Wells[31] has suggested that the structure is better described as an aggregate of mercuric chloride molecules, chloride ions, and ammonium ions. Similarly in $K_2HgCl_4.H_2O$, two mercury-chlorine distances are shorter than the other four, and it has recently been found that the structure is best represented as the double salt, $2KCl.HgCl_2.H_2O$.[32] Crystals of $CsHgCl_3$ were considered to have six chlorine atoms arranged equidistantly and octahedrally about each mercury,[31] however a recent redetermination of the structure has shown that the compound is the double salt, $CsCl.HgCl_2$.[32]

The structures of Ag_2HgI_4 and Cu_2HgI_4, proposed on the basis of an early X-ray investigation[33], have to be modified.[34] Crystals of these complexes were considered to contain Cu^+ or Ag^+ ions and $HgI_4{}^{2-}$ ions. Recent structural studies have shown that the unit cell contains two formula units[34] and not one as previously supposed.

Barker and Porter examined the morphology of a number of quaternary iodomercurates,[13] but no full structural determination has been made. Crystals of the analogous complex, bis(tetramethylammonium) tetrachlorozincate(II) have been shown to contain $ZnCl_4^{2-}$ ions.[35]

Magnetic Properties.

Cuprous, argentous, and thallous tetraiodomercurates were found to be diamagnetic at room temperature.[5] However recent investigations have shown that these compounds show a weak, nearly temperature independent paramagnetism, after correction for the diamagnetism of the ions.[36] The magnetic properties of a number of quaternary iodomercurates are reported in Chapter 2.

Infra-red Spectra.

The infra-red spectra of a number of sulphonium iodomercurates have been determined and compared with the uncomplexed sulphonium iodides.[37] Bands have been attributed to C-H stretching and bending modes, and a band characteristic of the C-S bond has been identified. In Chapter 2 the infra-red spectra of tetramethylphosphonium iodide and the various tetramethylphosphonium iodomercurates are discussed.

Aqueous Decomposition Reactions.

Alkali metal and ammonium iodomercurate(II) complexes decompose to mercuric iodide when treated with water.[12,15] François found that pyridinium iodomercurates undergo partial decomposition to mercuric iodide when treated with water.[15] Lal Datta[12] observed that quaternary ammonium iodomercurates deepened in colour when washed with water, and suggested that the decompositions gave octaiodotrimercurate complexes, as his experiments had shown that the latter complexes were prepared in precipitation reactions, when *dilute* aqueous solutions of a quaternary ammonium iodide and mercuric chloride were mixed. Bis(triethylsulphonium) tetraiodomercurate(II) decomposes to the tri-iodomercurate, diethylsulphide, and ethyl iodide on heating with water.[10] The exact nature of the aqueous decomposition reactions of tetramethylammonium, pyridinium, tetramethylphosphonium, and triphenylmethylarsonium iodomercurate(II) complexes have now been elucidated, and the results are presented in Chapter 2.

Thermal Decomposition Reactions.

Balfe, Kenyon, and Phillips[10] studied the effect of heat on a number of sulphonium iodomercurate(II) complexes. These reactions may be summarised by the equations,

$$[Et_3S]_2[HgI_4] \longrightarrow [Et_3S][HgI_3] + Et_2S + EtI$$

$$[PhEt_2S]_2[HgI_4] \longrightarrow [PhEt_2S][HgI_3] + PhEtS + EtI$$

$$3[PhEt_2S][HgI_3] \longrightarrow [PhEt_2S]_2[Hg_3I_8] + \ ? \ .$$

The volatile products were not examined in the latter reaction, but were probably phenylethylsulphide and ethyl iodide.

Solution Properties of Halomercurate(II) Complexes.

The solubilities of anionic halomercurate(II) complexes vary considerably with the associated cation. The advantages of quaternary cations in the study of anionic metal halide complexes are that the complexes of these cations may readily be prepared by precipitation reactions and are generally soluble in polar organic solvents.[38]

Species Detected and Their Stability Constants.

Until the systematic studies of Sillén,[39-42] there was considerable uncertainty as to the halomercurate species present in aqueous solution. There was even greater confusion as to the stability constants of the species detected. The results of these early studies have been previously reviewed.[39]

Sillén and his co-workers[39-42] have shown that the equilibrium between Hg^{2+} and X^- (where X is Cl, Br, I) in aqueous solution can be described by the formation of HgX^+, HgX_2, HgX_3^- and HgX_4^{2-}, and that there is no need to postulate the formation of polynuclear species. A recent study of the formation of halomercurate complexes in acetonitrile by means of conductivity measurements has demonstrated the formation of the complexes HgX_3^-, HgX_4^{2-}, and $Hg_2X_5^-$ (where X is Cl, Br, I) in this solvent.[4] Aggarwal[43] has investigated complex formation between mercuric chloride and ammonium chloride, and between mercuric bromide and potassium bromide in water by a continuous variation method, using depression of freezing point, conductance, viscosity, and density measurements. The formation of $HgCl_3^-$, $HgCl_4^{2-}$, and $HgBr_4^{2-}$ was demonstrated in the respective systems. However the range of concentration ratios used in the chloride system was too small to investigate the possibility of formation of $Hg_2Cl_5^-$, and in the bromide system the solubility of mercuric bromide was too low to permit the formation of the $HgBr_3^-$ ion to be studied.

A selected list of stability constants for the various halomercurate complexes is given in Table 1.2. Most recent results are given, together with early results that are now confirmed. In aqueous

TABLE 1.2

Stability Constants of Halomercurate Complexes[44]

log K_n refers to the reaction: $[\mathrm{HgX}_{n-1}]^{3-n} + \mathrm{X}^- \rightleftharpoons [\mathrm{HgX}_n]^{2-n}$,

where n is 1-4.

thus $\log K_n = \log \dfrac{[(\mathrm{HgX}_n)^{2-n}]}{[(\mathrm{HgX}_{n-1})^{3-n}][\mathrm{X}^-]}$ where X is F, Cl, Br, I.

log K_p refers to the reaction: $\mathrm{HgX}_3^- + \mathrm{HgX}_2 \rightleftharpoons \mathrm{Hg}_2\mathrm{X}_5^-$

thus $\log K_p = \log \dfrac{[\mathrm{Hg}_2\mathrm{X}_5^-]}{[\mathrm{HgX}_3^-][\mathrm{HgX}_2]}$ where X is Cl, Br, I.

Ligand	Temp.	Solvent	log K_1	log K_2	log K_3	log K_4
F^-	25°	water*	1.03			
Cl^-	25°	water*	6.74	6.48	0.85	1.00
Cl^-	25°	water*	6.74	6.48	0.95	1.05
Cl^-	25°	water	6.8	6.6	0.57	1.46
Cl^-	25°	water			0.70	
Cl^-	25°	MeCN	(log K_p = 0.70)		6.00	2.23
Br^-	25°	water*	9.05	8.28	2.41	1.26
Br^-	25°	water*	8.94	7.94	2.27	1.75
Br^-	25°	water	9.40			
Br^-	15°	water*			2.36	1.41
	25°				2.13	1.36
	35°				2.04	1.26
Br^-	25°	MeCN	(log K_p = 1.0)		6.00	2.04
I^-	25°	water*	12.87	10.95	3.78	2.23
I^-	25°	water*	12.87	10.95	3.67	2.37
I^-	25°	water*			3.70	2.16
I^-	25°	MeCN	(log K_p = 1.0)		5.95	1.61
	50°		(log K_p < 1.0)		5.85	1.48

* Ionic strength constant.

solution the stability constants of Sillén[39-42] and those of Marcus[45] must be taken as definitive. There is some disagreement between the results for the bromo complexes. As Sillén and Marcus used different experimental methods, Marcus reinvestigated the stabilities of the bromo complexes using the method of Sillén (e.m.f. method) and showed that Sillén's results were incorrect. The stabilities obtained by these workers for chloro and iodo complexes agree closely.

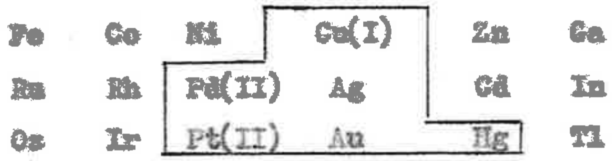
It can be seen from Table 1.2 that the stabilities of the halomercurate complexes in aqueous solution increase from HgF_n^{2-n} to HgI_n^{2-n} (where n is 1-4). Mercury is one of a small group of elements whose halide complexes show this stability pattern.[1] These elements are given in Table 1.3. For the majority of elements forming these complexes, the stability decreases from fluoride complexes to iodide complexes. The reasons for the sequence observed with mercury are considered after bonding in halomercurate(II) complexes has been discussed. The data of Ellendt and Cruse[4] for the stabilities of halomercurate complexes in acetonitrile suggest that in this solvent the stability sequence for tetrahalomercurates is chloromercurates > bromomercurates > iodomercurates. The differences in stability between the various trihalomercurates is small. As the method used is less accurate than that used for the determination of stability constants in water it would be unwise to attach any theoretical significance to these results.

Ultra-violet Spectra.

Only the spectra of iodomercurate(II) complexes are considered. The results of earlier workers are given in Table 1.4. Gallais[54]

TABLE 1.3

Stability Pattern for Metal Halide Complexes[1]



Fe	Co	Ni	Cu(I)	Zn	Ga
Ru	Rh	Pd(II)	Ag	Cd	In
Os	Ir	Pt(II)	Au	Hg	Tl

The enclosed elements form metal halide complexes with the stability sequence $F < Cl < Br < I$.

TABLE 1.4

Ultra-violet Spectra of Iodomercurate Species

Complex	Solvent	Remarks	max(Å)	log e	Ref.
HgI_2	H_2O		2650 2100	3.66 -	46,57
HgI_2	EtOH		2720	3.75	46
HgI_2	EtOH		2700	3.30	47
HgI_2	EtOH		2740	3.30	48
HgI_2	EtOH		2730 2150	3.74 4.36	49
HgI_2	MeOH		2680	3.30	50
HgI_2	$CHCl_3$, CCl_4, Bu^tOH		2750	-	51
HgI_2		vapour	2660 2240		52
HgI_2		vapour	2680 2240		53
$HgI_3 \cdot H_2O$(?)	aqueous EtOH 20% EtOH	$KHgI_3 \cdot H_2O$ used	ca.2980 ca.2580	ca.4.0 ca.4.1	54 *
HgI_4^{2-}(?)	aqueous EtOH 20% EtOH	K_2HgI_4 used	ca.3030 ca.2480	ca.3.9 ca.3.9	54 *
HgI_4^{2-}	water	HgI_2/KI**	3230 2670	4.37 4.51	46
HgI_4^{2-}	EtOH	HgI_2/NaI**	3290 2730	4.28 4.39	46
HgI_4^{2-}	water	HgI_2/XsKI	3210 2260	4.40 4.66	55

* Measured by G.B.D. from diagrams in text.

(?) Allocation of bands to these species possibly wrong (see text).

** Concentration of each component given in original reference. The system in water was studied over a wide concentration range.

assumed that solution composition and the solid state stoichiometry were the same, e.g., that $KHgI_3.H_2O$ gave $HgI_3.H_2O^-$ ions in solution. Results to be presented (Chapter 3) show that this assumption is often incorrect with iodomercurate complexes, hence assignments on the basis of this assumption are uncertain. The maxima given for HgI_4^{2-} are certainly wrong as they disagree with the results of Fromherz and Lih,[46] which were obtained from studies over a wide concentration range. These workers found that the lower wavelength maximum of the tetraiodomercurate ion has the same position as the higher wavelength maximum of mercuric iodide. However the extinction coefficient obtained for the tetraiodomercurate ion is considerably greater than that observed for mercuric iodide, and hence the maximum was attributed to the tetraiodomercurate ion. The maximum observed by Tsuchida[55] at 2260 A is undoubtably due to the absorption of free iodide ions, which have a maximum at 2260 A in aqueous solution (measured at 20°).[56] The failure to observe a third band for the tetraiodomercurate ion was considered theoretically significant,[55] but the absence of the band at 2670 A, observed by Fromherz and Lih,[46] may simply be due to the masking of this maximum by iodide ions (present in excess). In fact the results of Fromherz and Lih[46] show that this is possible.

The results of studies of the ultra-violet spectra of quaternary iodomercurate(II) complexes in ethanol and methanol are presented in Chapter 3. The aim of this work was to identify the iodomercurate species present in solutions of members of each stoichiometric class of the quaternary iodomercurates, and to obtain the spectrum of the triiodomercurate ion. Since this work was completed, Griffiths and Symons[57] have reported the spectrum of the tri-iodomercurate ion in a number of solvents, excluding methanol and ethanol. Their results are discussed during the presentation of the original work in Chapter 3.

The Nature of the Ultra-violet Absorption Bands of Iodomercurate(II) Complexes.

The positions of the bands and their intensities show that they are caused by charge transfer processes.[58] On the basis of a theoretical treatment, Balhausen suggests that attempts to distinguish between the possible directions of charge transfer, viz., metal ⟶ ligand or ligand ⟶ metal is frequently pointless.[59] However, with halomercurate(II) complexes, as with haloferrate(III) and with halopentammine-cobalt(III) complexes, the charge transfer bands move to longer wave-lengths (lower energies) as the halide ligands become more readily oxidised. This is what would be expected for ligand to metal electron transfer, or more precisely for the transfer of an electron from a molecular orbital largely concentrated on the ligand to one largely concentrated on the metal.[58,60]

The spectra of alkali metal halide ion pairs in the gas phase and in solution are consistent with the transfer of an outer p electron of the halide ion to the outer s orbital of the metal atom during light absorption. In general two bands are found with an energy separation approximately equal to the energy separation between the $^2P_{3/2}$ and the $^2P_{1/2}$ states of the halogen atoms.[51,57] Thus the charge transfer process corresponds to the reaction $[M^+X^-] \rightleftharpoons M + X$ (where M and X are alkali metal and halogen atoms respectively). Katzin[51] has shown that many halogen containing compounds have spectra containing a similar pair of bands, and proposed that halogen atoms are formed in the excited states of all these compounds. While in some cases the charge transfer process is accompanied by the production of free radicals or atoms, e.g., $Fe^{3+} + Cl^{-} \longrightarrow Fe^{2+} + Cl$,[60] it is not necessary for such a process to result in dissociation, as completely stable intermediates may well be formed.[61] For halogen containing compounds some indication as to whether halogen atoms are formed during light absorption can be obtained from a comparison of the theoretical energy separation between the $^{2}P_{3/2}$ and $^{2}P_{1/2}$ states of the halogen atoms and the experimental separations between the two charge transfer bands. Such a comparison is made for the iodomercurate(II) complexes in Chapter 3. If light absorption by mercuric iodide is accompanied by the formation of iodine atoms, the process may be represented by the equation $HgI_2 \rightleftharpoons HgI + I$. Griffiths and Symons[57] list a number of objections to such a mechanism for mercuric iodide. It is sufficient to consider one of these. Since covalent bonding is important in mercuric iodide (see section on structure and bonding in halomercurate(II) complexes), it may be expected that the charge transfer process involves p_{π} electrons of the iodine atom rather than the more tightly held σ electrons. Thus it is difficult to see how iodine atoms could be formed during the act of light absorption.[57] It is probably more correct to represent the transition undergone by mercuric iodide by the reaction $I — Hg^{II} — I \rightleftharpoons I — Hg^{I} — I^{+}$. It is suggested that the transitions involve the transfer of a p_{π} electron from an outer π_g orbital essentially localised on the iodine to a π_u orbital essentially localised on the mercury.[57]

Conductivity Properties.

The use of conductivity measurements in the determination of stability constants of various halomercurate complexes in acetonitrile has already been mentioned.[4] Cavell and Sugden[17] studied the conductivity of a number of quaternary ammonium and sulphonium tri-iodomercurates in acetone in the concentration range 10^{-2}-10^{-4} M and showed that the compounds were 1:1 electrolytes. Triethylphenylammonium pentaiododimercurate(II) was also shown to be a 1:1 electrolyte. Recently the conductivities of mercuric iodide, tetraethylammonium iodide, and a mixture of the two compounds in the ratio of 1:2 have been measured in N,N dimethylformamide.[62] The tetraiodomercurate complex was considered to be present in the latter system.

Conductivities of a number of quaternary iodomercurates in acetone have been measured in the concentration range 10^{-3}-10^{-6} M. The investigation of more dilute solutions than have been previously examined has provided considerable information concerning the behaviour of iodomercurate complexes in this solvent. These results are presented in Chapter 3, together with a critical discussion of the interpretation of the conductivity measurements of earlier workers.[17,62]

Reactions in Solution.

The tetraiodomercurate and tri-iodomercurate complexes of the *l*-phenacylethylmethylsulphonium cation have been prepared and their racemization studied.[10] The rate of racemization in acetone of the tri-iodomercurate complex was found to be much slower than that of the tetraiodomercurate complex. The racemization of optically active sulphonium halides is believed to be due to the existence of the equilbrium $RR'R''S^+ + X^- \rightleftharpoons RR'S + R''X$ (X is a halogen). The results of the racemization reactions of the iodomercurate complexes were interpreted as indicating greater dissociation of the tetraiodomercurate complex into free sulphonium iodide than the tri-iodomercurate. Thus the tri-iodomercurate complex was considered more stable than the tetraiodomercurate complex in this solvent. The racemization of tris(l-phenacylmethylethylsulphonium) heptachlorodimercurate(II) in methanol was also studied.[10]

In Chapter 3 the reactions of the various stoichiometric classes of the quaternary iodomercurates with triphenylphosphine in acetone solution are discussed. This investigation arose from an unsuccessful attempt to prepare the complex $[PyH][Ph_3P.HgI_3]$. Analogous nickel complexes have been prepared.[63]

The Structure of Halomercurate(II) Complexes in Solution.

(1) The ions HgX^+ (where X is a halogen).

X-ray studies of solutions containing the $HgCl^+$ ion have been made.[64] The results suggest that the ion is present as the tetrahedral species $HgCl(H_2O)_3{}^+$, rather than as the octahedral $HgCl(H_2O)_5{}^+$. It has been also suggested that the ion HgI^+ exists in aqueous solution as the linear species $HgI(H_2O)^+$,[57] as the ultra-violet maximum tentatively assigned to HgI^+ (2450 Å) is of similar intensity to the maximum of MeHgI (2300 Å).[49] As the latter argument is by no means conclusive and as the interpretation of the X-ray measurements is not certain, the structure of HgX^+ complexes remains in doubt.

(2) The complexes HgX_2 (where X is a halogen).

Mercuric iodide undergoes partial disproportionation in

N,N dimethylformamide,[57] $2HgI_2 \rightleftharpoons HgI^+ + HgI_3^-$. However the higher wavelength maximum of mercuric iodide in the majority of solvents corresponds closely with that found for the spectrum of the vapour (Table 1.4), from which it is concluded that in solution mercuric iodide is present as the linear unionized molecules, as in the vapour state.[65] In confirmation of this, the Raman band of mercuric iodide in a number of solvents[66] is very close to that found for mercuric iodide vapour.[67] There is also spectral evidence to show that mercuric bromide is linear and unionized in ethanol and water.[46] As the ultra-violet and Raman spectra of mercuric iodide in solution and in the vapour correspond so closely, it has been suggested that no solvent is coordinated to mercuric iodide in solution.[57] This proposal is not convincing as the addition of ammonia, which should at least coordinate weakly, to solutions of mercuric halides does not produce a change in the ultra-violet absorption maxima.[49] Thus while the spectral studies establish the configuration of the halide ligands about mercury, no information is provided as to whether solvent molecules are also weakly bound. X-ray studies of solutions of mercuric chloride in water have shown that the octahedral species $HgCl_2(H_2O)_4$ is present in solution, the two chlorines occupying trans positions.[64] The mercury-oxygen bond distances appear to be larger than in $Hg(H_2O)_6^{2+}$.[64]

(3) The complexes HgX_3^- (where X is a halogen).

It has been proposed that the tribromomercurate ion is present in aqueous solution as the ion, $HgBr_3.H_2O^-$, on the basis of Raman spectra measurements.[68] Such a species has also been postulated to explain why the observed entropy of the tetrabromomercurate ion exceeds that of the tribromomercurate, when the calculated entropies show the reverse order.[69] Gallagher and King[70] found that the entropy of the trichloromercurate ion was best explained by assuming $HgCl_3(H_2O)_3^-$ to be present in aqueous solution, and suggested that the same was true of the tribromo and tri-iodo complexes. X-ray investigation of the aqueous trichloromercurate species has not given an unequivocal answer to the problem. The species $HgCl_3(H_2O)_2^-$ was considered possible.[71]

(4) The complexes HgX_4^{2-} (where X is a halogen).

Raman spectra studies of the tetrachloromercurate ion in aqueous solution indicate that this complex has regular tetrahedral structure.[68] Some distortion of the tetrahedral structure was suggested by X-ray diffraction of this complex in aqueous solution.[64] The X-ray diffraction of aqueous tetraiodomercurate solutions is consistent with the complex having a regular tetrahedral structure.[64] The mercury-iodine bond distance found is considerably shorter than the sum of the ionic radii, and agrees almost exactly with the sum of the covalent radii. Due to the empirical nature of the latter it is not necessarily true that the bonds are essentially covalent because of this agreement.[72] However the observed mercury-iodine bond distance closely agrees with that found for solid mercuric iodide* in which the bonds are probably largely covalent, therefore it is reasonable to assume that the bonds in the tetraiodomercurate complex have considerable covalent character.

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* The mercury-iodine bond distance found for gaseous mercuric iodide cannot be used for comparison, as the bonds have a linear arrangement about mercury. In solid mercuric iodide, the mercury-iodine bonds are arranged tetrahedrally about the mercury.[31]

The Bonding in Halomercurate(II) Complexes in Solution.*

Bonding in tetrahalomercurate(II) complexes is considered first, as there is least disagreement as to the structure of these complexes. It was suggested in the foregoing section that the bonds in these complexes have considerable covalent character, hence it is best to use the molecular orbital theory in a discussion of the bonding. However the application of the molecular orbital theory to tetrahedral complexes is more complicated than for octahedral or planar complexes,[73] and is only briefly discussed.

The mercury orbitals that must be considered are the 5d, 6s, and 6p orbitals. For convenience four sets of orbitals are listed in Table 1.5.

TABLE 1.5

Sets of Orbitals of the Hg^{2+} Ion

(a) s, p_x, p_y, p_z

(b) $s, d_{xy}, d_{yz}, d_{xz}$

(c) $d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$

(d) $p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$

where $d = 5d$, $s = 6s$, $p = 6p$; d_{xy}, d_{yz}, d_{xz} are d_ε orbitals, $d_{z^2}, d_{x^2-y^2}$ are d_γ orbitals.

Set (a) or set (b) can be used for σ bond formation. The use of set (a) corresponds approximately to the use of sp^3 hybridization in the terminology of the valence bond theory. Quite likely in practice d-p mixing occurs, and thus three d-p hybrids and an s orbital of the metal are used for σ bond formation.[73,74] These are combined with

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* In this discussion fluoromercurates are not considered, as these complexes appear unstable in solution (Table 1.2).

appropriate orbitals of the halide ligands to give four bonding and four antibonding orbitals. Eighteen electrons have to be accommodated (ten originally from the d orbitals of the mercuric ion, and eight originally occupying halide ion orbitals - two from each halide ion). Eight of these electrons occupy the four bonding orbitals, six the three d-p hybrids not used for σ bond formation, and four the d_γ orbitals.

The possibility of π bond formation between filled metal orbitals and empty orbitals of the ligands must now be considered. It has been stated on several occasions that two weak and two strong π bonds can be formed in tetrahedral complexes.[75] This has recently been contradicted.[74] If set (a) are used for σ bond formation, then set (c) are available for π bond formation, and it has been shown[76] that the d_ε orbitals have the same overlap with the ligand π orbitals as the d_γ orbitals. If set (b) are used for σ bond formation, then set (d) are available for π bond formation. It is considered that there is no reason why there should be a major difference in strength between π bonds formed by the p orbitals and those formed by the d_γ orbitals.[74] With the use of d-p hybrids for σ bond formation, three d-p hybrids and the d_γ orbitals are available for π bond formation, and there is no reason to consider the interaction of the former negligible compared with the latter.[74]

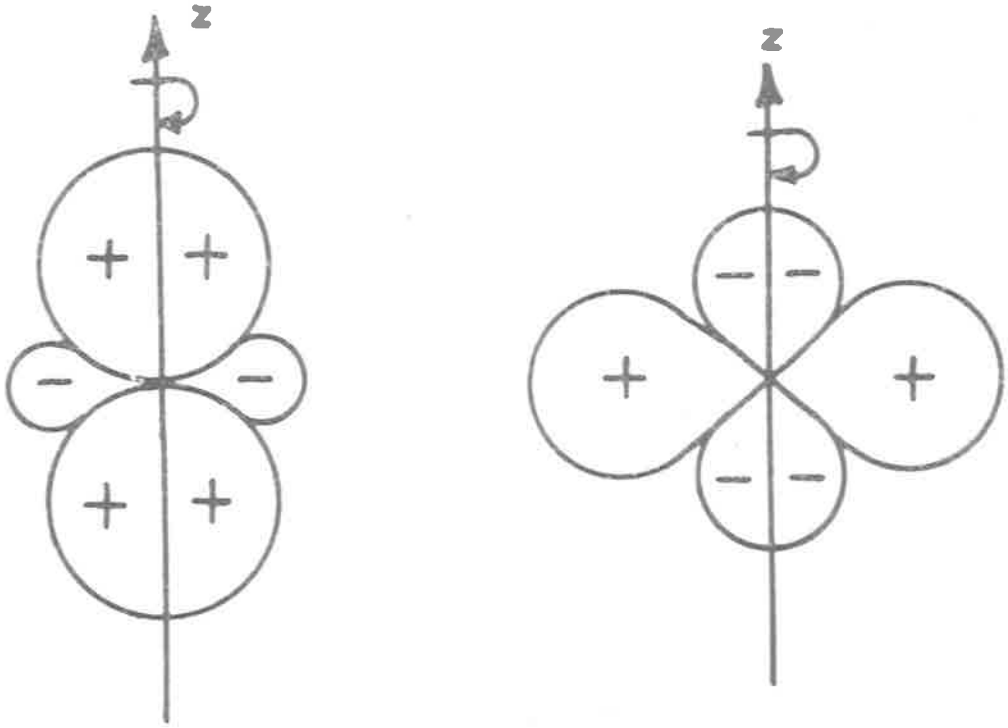
The crystal field theory does not assist greatly in understanding the bonding in these complexes. It predicts a splitting of the d orbitals into an upper triplet d_ε and a lower doublet d_γ, and no crystal field stabilization energy for complexes of d^{10} metal ions.

Few conclusions can be drawn concerning bonding in trihalomercurate(II) complexes due to the uncertainty as to the structure of the trihalomercurate ions in solution. The mercury-halogen bonds probably have considerable covalent character as do those of the tetrahalomercurate complexes. It is possible that these bonds would be arranged trigonally in a non-coordinating solvent, though dimerisation to give $Hg_2X_6^{2-}$ (where X is a halogen) may occur to give mercury its more common coordination number of four. In a coordinating solvent the species $HgX_3.S^-$, $HgX_3.S_2^-$, or $HgX_3.S_3^-$ (where S is a solvent molecule) are possible. The choice of coordination number will be largely dependent on the polarisability of the solvent molecules. In an easily polarised solvent, tetrahedral four coordination will be favoured in accordance with the Pauling electroneutrality principle,[77,78] as the mercury-solvent bond will have partial covalent character; the stereochemistry will thus be dictated by the repulsion between the three mercury-iodine bond pairs and the mercury-solvent bond pair. (Analogous arguments have been used to explain why four is the preferred coordination number in complexing between the d^{10} ion, Zn^{2+}, and halide ligands, whereas six is preferred with water as the ligand.[78]) In a less readily polarised coordinating solvent the coordination number five is possible. Three mercury-halogen bonds could be arranged trigonally in the XY plane, with two longer electrostatic mercury-solvent bonds in the Z direction.

The mercuric dihalides are considerably more stable than the analogous cadmium and zinc compounds. In general two coordinate complexes of heavy metals with a d^{10} configuration have considerable stability. Two explanations have been given. Frequently this has been attributed to the use of sp hybrid bonds by the metal. An alternative crystal field approach has been suggested by Orgel.[79] The stability of two coordination can be explained by d-s mixing, which is energetically more favourable for the third transition series than the first or second if the positive charge on the metal is high.[78,79] Hybridisation of the d_{z^2} and s orbitals gives two new orbitals shown in Fig. 1.1. If the two electrons are put into the hybrid orbital (a), the metal develops a strong electronegativity in the xy plane and can form four short bonds in this plane, whereas if the electrons are placed in the orbital (b), the metal develops a strong electronegativity in the z direction with the formation of two short bonds. In practice the latter arrangement seems preferred.[79] Where the charge on the metal ion is low it is preferable to explain the two coordination in terms of sp hybrid formation.[78] In the mercuric dihalides the mercury-halogen bonds are largely covalent, hence the formal charge on the mercury must be low, and sp hybridization should be important. Nyholm, however, has shown that the two approaches to two coordination in the third transition series are not as dissimilar as might appear at first sight;[78] thus the linear orbitals used by mercury in the mercuric dihalides might be considered hybrids of p orbitals and the sd hybrid, orbital (b) in Fig. 1.1.

The uncertainty as to the structure of the HgX^+ ions (where X is a halogen) in solution precludes a discussion of the bonding. Whether $HgX(solvent)^+$ or $HgX(solvent)_3{}^+$, the two most likely species in solution, predominates in a given solvent will largely depend on the polarizability of the solvent molecules.

Fig. 1.1. Hybrid Orbitals Formed From the d_{z^2} and s Orbitals.



(a) $\frac{1}{\sqrt{2}}(d_{z^2}+s)$

(b) $\frac{1}{\sqrt{2}}(d_{z^2}-s)$

The Stability Sequence of Halomercurate(II) Complexes.

It is now possible to explain the stability sequence observed for halomercurate complexes. The relative stabilities of the halide complexes of elements outside the enclosed group in Table 1.3 is as expected if complex formation is due to essentially electrostatic forces.[80] Strong bonds are to be expected with ligands having slight polarizability and a small ionic radius. Both these factors decrease from iodide to fluoride, the difference between chloride and fluoride being marked. This would give a stability sequence for the metal halide complexes, $F^- \gg Cl^- > Br^- > I^-$, as found.[80] The reversal of this stability pattern for the halide complexes of the enclosed group of elements in Table 1.3 has been related to double bond formation.[1,80] The fluoride ion does not possess vacant d orbitals in its outer valence shell, hence is unable to participate in π bonding with the available filled metal orbitals, whereas chloride, bromide, and iodide can. This should lead to a substantial difference in stability between the fluoride complexes and those of the other halide ions if stability is related to double bond formation. As the metal-halide bonds of the complexes of elements in the enclosed group have considerable covalent character, the strength of the metal-ligand σ bond depends on the polarizability of the halide ligand, which increases from fluoride to iodide. These two factors should give a stability sequence, $F^- \ll Cl^- < Br^- < I^-$, for metal halide complexes of the enclosed elements (thus including mercury),[80] as found. This stability sequence is also favoured by the solvation energies of the halide ions.[81]

Williams has suggested that the reversal of the normal stability pattern for metal halide complexes amongst the enclosed elements (Table 1.3) is not due to π bond formation, but is due to the high polarizing power of the cations involved.[82] The function chosen by Williams to distinguish between the two classes of cations forming metal halide complexes has been criticised by Westland.[83] From a consideration of thermochemical data, he considers that π bonding is unimportant for the binary halides and sulphides of the third period transition metals. He concludes that extensive π bonding is only likely in complexes in which the formal charge on the metal is zero or negative. (Tri- and tetrahalomercurate(II) complexes are of course within this classification.) Some of the factors influencing the formation of double bonds by ions or atoms with the d^{10} configuration have been discussed by Nyholm.[78] In particular it has been shown that the ability of the Hg^{2+} ion to form π bonds is less than that of Pt^{0}, and that decreasing the formal charge on the d^{10} ion or atom increases the likelihood of π bond formation.[78] Thus the possibility of π bonding should increase in the sequence HgI_2, HgI_3^-, HgI_4^{2-}. Promotion energies and ionization energies[78] indicate the possibility of π bonding should be greater for the mercuric ion than for either Zn^{2+} or Cd^{2+}.

B. The Chemistry of Halo(tertiary phosphine and arsine)mercury(II) and -cadmium(II) Complexes.

The complexes of mercuric halides with tertiary phosphines and arsines belong to five stoichiometric classes, viz., 1. B_2HgX_2, 2. $B.HgX_2$, 3. $B_3(HgX_2)_2$, 4. $B_2(HgX_2)_3$, and 5. $B(HgX_2)_2$ (where B represents either tertiary phosphines or tertiary arsines in classes 1-4, and tertiary arsines in class 5, and X is Cl, Br, I in classes 1-3, 5, and is I in class 4).[84] Cadmium halides form complexes with tertiary arsines and phosphines corresponding to three stoichiometric classes, viz., 1. B_2CdX_2, 2. $B.CdX_2$, and 3. $B_3(CdX_2)_2$ (where B and X have the same meanings as in classes 1-3 of the mercuric halide complexes.)[84]

Structure, Bonding, and Reactions.

The structures of the various stoichiometric classes of the halo(tertiary phosphine and arsine)mercury(II) and -cadmium(II) complexes are given in Fig. 1.2.

1. B_2MX_2*

The structures of the solid complexes have not been determined, however it is certain that the ligands are arranged in an approximately tetrahedral configuration about the central metal (Fig. 1.2, structure 1).[84] The complexes behave as non-electrolytes in solution[85] and their molecular weights in solution correspond closely to that required by the proposed structure.[84,85]

2. $B.MX_2$

An X-ray investigation of the solid complexes has shown that the compounds possess a centre of symmetry. This necessitates the postulation of the trans bridged structure (Fig. 1.2, structure 2), the ligands being distributed tetrahedrally about mercury or cadmium.[84] This has been confirmed by the detailed investigation of the structure of

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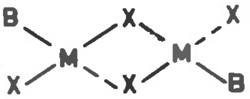
* The abbreviations used in the discussion of this and subsequent stoichiometric classes of these complexes are explained in Fig. 1.2.

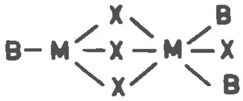
Fig. 1.2. Structures of Halo(tertiary phosphine and arsine)-mercury(II) and -cadmium(II) Complexes.

1. B_2MX_2

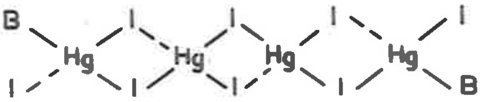
2. $B\cdot MX_2$



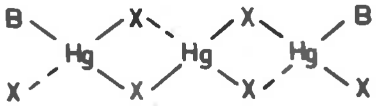
3. $B_3(MX_2)_2$



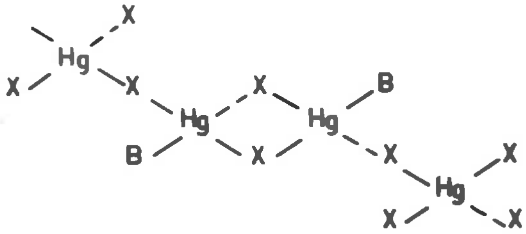
4. $B_2(HgI_2)_4$



5. $B_2(HgX_2)_3$ (a)



(b)



Nos. 1-3 M is Cd and Hg; X is Cl, Br, and I.

Nos. 1-4 B represents tertiary phosphines and arsines.

No. 5 (a) B is Et_3As; X is I.

(b) B is $Pr_3{}^nAs$, and X is Cl, or B is $Bu_3{}^nAs$, and X is Br.

the complex $(Et_3As.HgI_2)$.[84] In solution partial dissociation of the complexes to the monomeric form occurs, e.g., $(R_3P.HgI_2)_2 \rightleftharpoons 2R_3P.HgI_2$.[85] A number of the cadmium halide complexes have been found to be monomeric in acetone or ethanol solution, presumably due to competitive coordination by the solvent. In general, association to give the dimer increases in solution as the polarity of the solvent decreases.[85] Thus a number of mercuric halide complexes have molecular weights corresponding to the dimers in benzene, but dissociate appreciably in acetone. The compounds are non-electrolytes in solution.[85]

3. $B_3(MX_2)_2$

X-ray diffraction shows that the complexes are not molecular lattices of the complexes B_2MX_2 and $B.MX_2$. A suggested structure is given in Fig. 1.2, structure 3, with alternate tetrahedral and octahedral arrangements of the ligands about the metal ions.[84] These complexes dissociate in solution.

4. $B_2(HgI_2)_4$

These complexes may either be molecular lattices of the 1:1 complexes and mercuric iodide or have the structure shown in Fig. 1.2, structure 4.[84]

5. $B_2(HgX_2)_3$

Two distinct structures have been found for these complexes. The compound $(Et_3As)_3(HgI_2)_2$ is yellow and has no centre of symmetry and a cis bridged structure has been proposed (Fig. 1.2, structure 5(a)).[84] The complexes $(Pr_3{}^nAs)_2(HgCl_2)_3$ and $(Bu_3{}^nAs)_2(HgBr_2)_3$ form colourless crystals, possess a centre of symmetry, and have been shown to have the structure, Fig. 1.2, structure 5(b),[84] with a distorted tetrahedral arrangement of ligands about mercury.

Bonding.

All the complexes except the $B_3(MX_2)_2$ class, the structures of which are still uncertain, have a tetrahedral arrangement of the ligands about the metal ions, and it may be concluded that the bonding is similar in each case. The metal-ligand bonds are probably largely covalent in character, thus the valence bond theory requires the use of sp^3 hybrid orbitals by the metal ions. A molecular orbital description of the bonding could be given and would be very similar to that previously given for the tetrahalomercurate(II) complexes. There is considerable chemical evidence for double bonding in complexes of phosphines to metal ions and atoms with filled d orbitals,[1,78,86] and it has been shown theoretically that considerable overlap can be obtained between these orbitals and the empty d orbitals of phosphorus.[87] A description of π bonding in these complexes is not given as it would be very similar to that already given for tetrahalomercurate(II) complexes, except that greater back coordination would probably occur to the phosphorus and arsenic atoms of the phosphine and arsine ligands than to the halide ligands.

Reactions.

It has been shown that di-iodobis(p-dimethylaminophenyldimethylphosphine)mercury(II) and di-iodobis(phenyldimethylphosphine)mercury(II) are converted to the corresponding bis(trimethylarylphosphonium) tetraiodomercurate(II) complexes by methyl iodide in acetone.[85] Analogous reactions of similar cadmium iodide complexes could not be achieved.[85] The reactions of the complexes $(Ph_3P)_n(HgX_2)$ (where n is

1 and 2, and X is Cl, Br, I) and $(Ph_3P)_2CdX_2$(where X is Br, I) with a number of alkyl halides have been studied in the present investigation, and the results are presented in Chapter 4. As halogen exchange has been found to occur in reactions where the halogens of the reactants differ, a study has been made of reactions of halomercurate(II) complexes, with alkyl halides containing a different halogen. These results are also given in Chapter 4.

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CHAPTER 2

Properties of Crystalline Group VB Quaternary Iodomercurate(II) Complexes

1. Preparations.[1]

The aim of the preparative work was to determine which of the four stoichiometric classes of the quaternary iodomercurate(II) complexes, viz., Q_2HgI_4, $QHgI_3$, $Q_2Hg_3I_8$, QHg_2I_5 (where Q is a univalent quaternary cation) could be isolated for the tetramethylammonium, pyridinium, tetramethylphosphonium, and triphenylmethylarsonium cations. Two general preparative methods were used, viz.:

(1) Reaction between the stoichiometric amounts of mercuric iodide and the quaternary iodide in acetone, the iodomercurate being isolated either quantitatively by evaporation to dryness, or in high yield after evaporation to crystallization.

(2) Addition of the stoichiometric amount of mercuric iodide, dissolved in excess aqueous potassium iodide, to the stoichiometric amount of the quaternary iodide, dissolved in water, when the required compound was precipitated in high yield. This method was found satisfactory for the preparation of tri-iodomercurate(II) and tetraiodomercurate(II) complexes, the product precipitated depending only on the ratio of mercuric iodide to quaternary iodide, and being independent of the presence of excess potassium iodide provided the reaction mixture was not heated. (The precipitation method can also be used with ethanol as the solvent for the reactants.)

The complexes isolated together with those reported by earlier workers are given in Table 2.1. The existence of the complex bis(tetra-

TABLE 2.1

Iodomercurate Complexes of Group VB Quaternary Cations

Compound	m.p. (°C)	
	This work	lit.
$[Me_4N]_2[HgI_4]$	> 300	not given[2]
$[Me_4N][HgI_3]$	243	236[3] > 200[4]
$[Me_4N][Hg_2I_5]$	189	-
$[Me_4N]_2[Hg_3I_8]$	*	not given[2]
$[PyH]_2[HgI_4]$	168	" " [2] 139[5]
$[PyH][HgI_3]$	149.5	151[5] 152-154[6]
$[PyH]_2[Hg_3I_8]$	101.5-102.5	101[5]
$[PyH][Hg_2I_5]$	*	121[5]
$[Me_4P]_2[HgI_4]$	> 300	-
$[Me_4P][HgI_3]$	197-197.5	-
$[Me_4P][Hg_2I_5]$	172	172[7,8,9]
$[Ph_3AsMe]_2[HgI_4]$	167	-
$[Ph_3AsMe][HgI_3]$	139-139.5	-
$[Ph_3AsMe][Hg_2I_5]$	*	-

* See text.

Compounds reported[2,5] were not recrystallised.

methylammonium) octaiodotrimercurate(II), previously reported,[2] could not be confirmed. A solid of this composition, m.p. 180°, was obtained on evaporation to dryness of an acetone solution of the stoichiometric amounts of mercuric iodide and tetramethylammonium iodide, but was separated into the tri-iodomercurate and the pentaiododimercurate on fractional recrystallization from acetone/ethanol. The existence of the complex pyridinium pentaiododimercurate(II)[5] could not be confirmed. A yellow-orange solid, m.p. ca. 130°, containing mercuric iodide in excess of that required for the formation of the octaiodotrimercurate, was isolated from ethanol, and may correspond to the pentaiododimercurate reported by François.[5] However when acetone was added to this substance, in an attempt to recrystallise, the immediate precipitation of red mercuric iodide occurred, while the octaiodotrimercurate went into solution. Even if further mercuric iodide is weakly bound to the octaiodotrimercurate, the bonding is not the same as in the other pentaiododimercurates prepared, which can be recrystallized unchanged. Attempts to prepare triphenylmethylarsonium pentaiododimercurate(II) resulted in the formation of a gluey product, which could be separated into the tri-iodomercurate and mercuric iodide.

It is tentatively concluded from the preparative work that a Group VB quaternary cation is unlikely to form both a pentaiododimercurate complex and an octaiodotrimercurate complex, and that large quaternary cations may form only tetraiodomercurate and tri-iodomercurate complexes. The size and shape of the quaternary cation apparently determine which complexes may be isolated. Possible structures of the crystalline complexes are considered later.

2. Magnetic Measurements.[1]

Approximate magnetic moments of a number of the iodomercurate complexes have been measured. The complexes $[PyH]_2[HgI_4]$, $[Me_4P][HgI_3]$, $[PyH]_2[Hg_3I_8]$, and $[Me_4N][Hg_2I_5]$ are diamagnetic. This is expected as the complexes are based on the mercuric ion, which has the configuration d^{10}. The diamagnetism of quaternary tetrahalozincate(II) complexes has been reported.[10]

3. Infra-red Spectra.

The infra-red spectra of the tetramethylphosphonium iodomercurates and bis(pyridinium) octaiodotrimercurate(II) have been measured in the region 500-2000 cm^{-1} (Fig. 2.1-2.4), using sodium chloride and potassium bromide optics. The compounds were examined as Nujol and hexachlorobutadiene mulls. Satisfactory spectra could not be obtained from 2000 cm^{-1} to 5000 cm^{-1}, due to the high background absorption of the complexes in this region.

For comparison with the spectra of the tetramethylphosphonium iodomercurates, the spectrum of tetramethylphosphonium iodide has been measured in the region 667-2000 cm^{-1} (Fig. 2.5), and shows satisfactory agreement with that obtained by West.[9]

The principal bands of the tetramethylphosphonium compounds together with those of trimethylphosphine[9] are given in Table 2.2. Where the spectra obtained with different optics overlap, satisfactory agreement has been obtained as to the positions of the maxima.

Mercuric iodide has no absorption bands in the region 500-1100 cm^{-1}, and bands are not expected for this compound in the 1100-2000 cm^{-1} region; metal-halide bonds only give low lying stretching frequencies

Fig. 2.1 - 2.5.

Infra-red Spectra of Quaternary Iodomercurates and Tetramethylphosphonium Iodide.

Fig. 2.1	The spectra of bis(tetramethylphosphonium) tetraiodomercurate(II) and tetramethylphosphonium tri-iodomercurate(II), obtained with sodium chloride optics.
Fig. 2.2	The spectra of the same compounds obtained with potassium bromide optics.
Fig. 2.3	The spectra of tetramethylphosphonium pentaiododimercurate(II) and bis(pyridinium) octaiodotrimercurate(II), obtained with sodium chloride optics.
Fig. 2.4	The spectra of the same compounds obtained with potassium bromide optics.
Fig. 2.5	The spectrum of tetramethylphosphonium iodide, obtained with sodium chloride optics.

The lower spectra for the region 6.5-7.5μ in Fig. 2.1, 2.3, 2.5 were obtained in hexachlorobutadiene. Other spectra were obtained in Nujol.

The maxima labelled N are due to Nujol.

Fig. 2.1

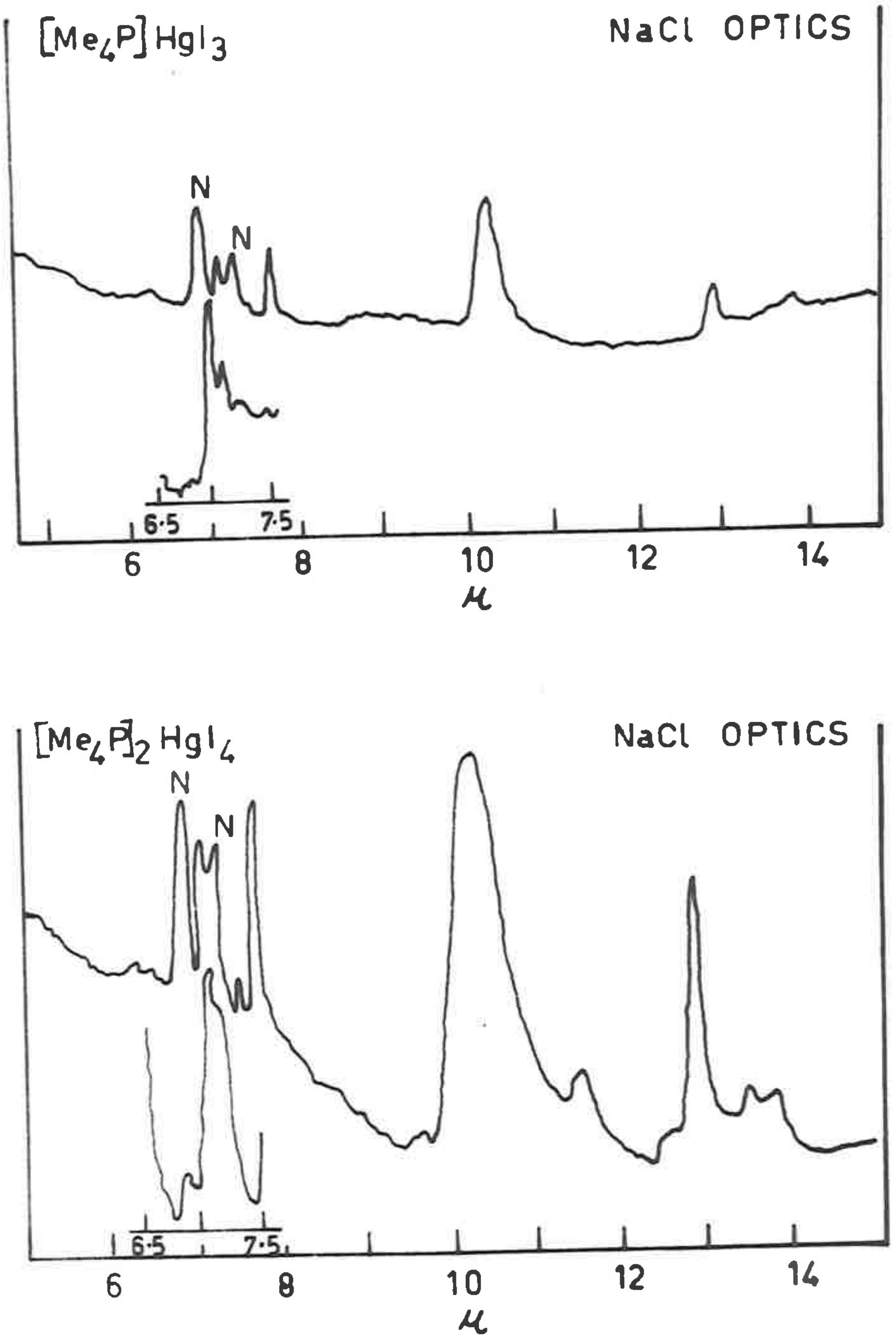

[Me$_4$P] HgI$_3$
NaCl OPTICS
N
N
6·5
7·5
6
8
10
12
14
μ
[Me$_4$P]$_2$ HgI$_4$
NaCl OPTICS
N
N
6·5
7·5
6
8
10
12
14
μ

Fig. 2.2

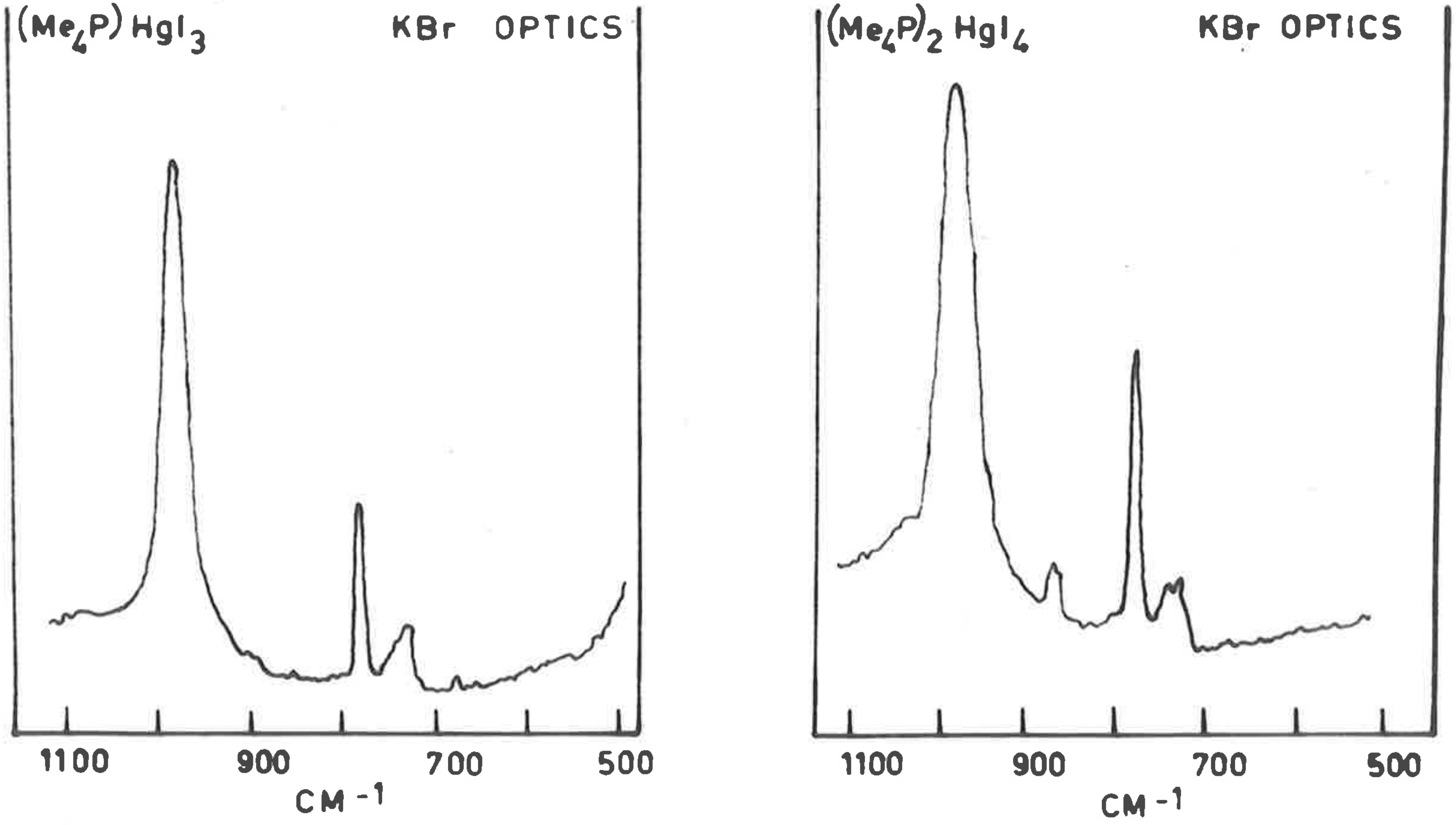

(Me4P) HgI3
KBr OPTICS
1100
900
700
500
CM -1
(Me4P)2 HgI4
KBr OPTICS
1100
900
700
500
CM -1

Fig. 2.3

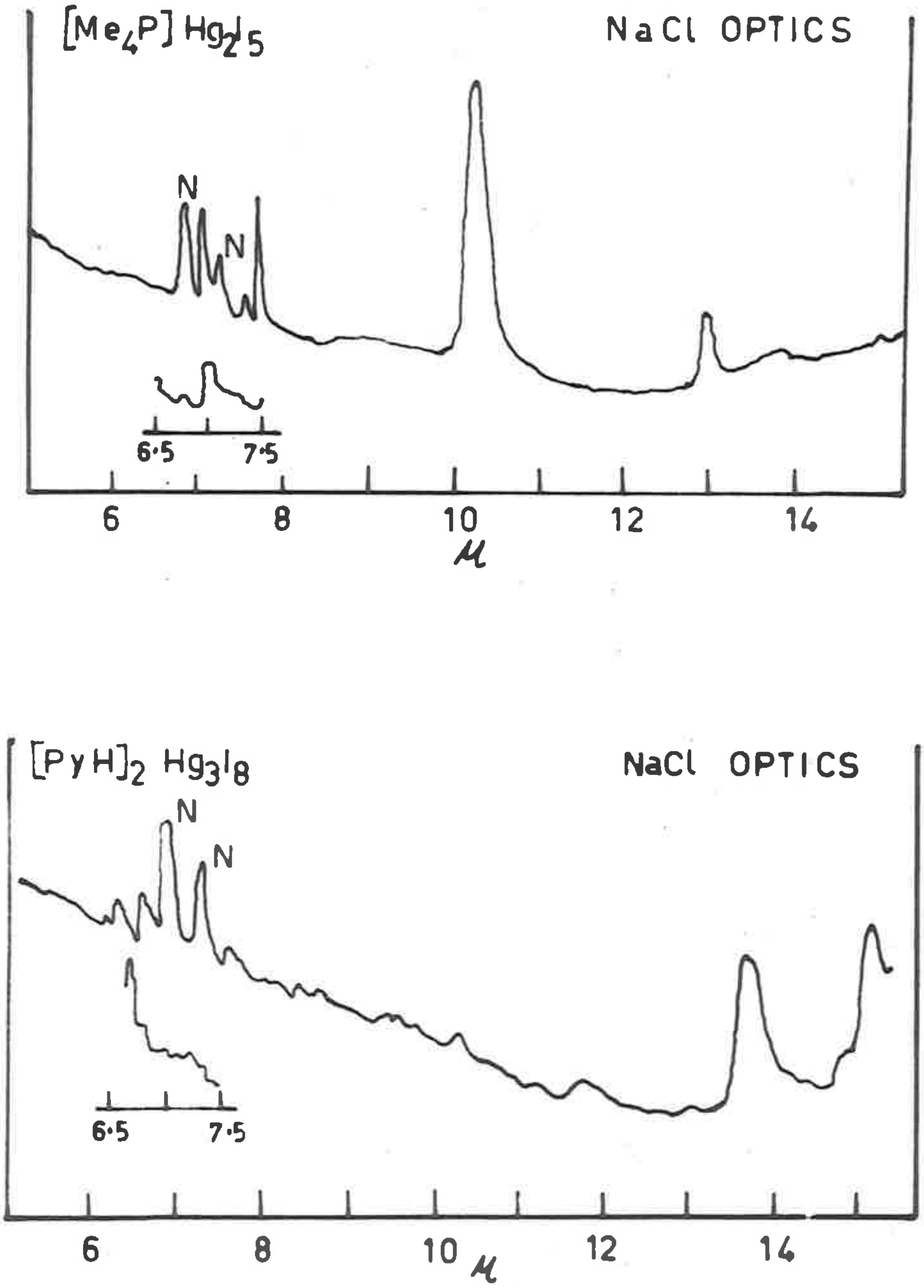
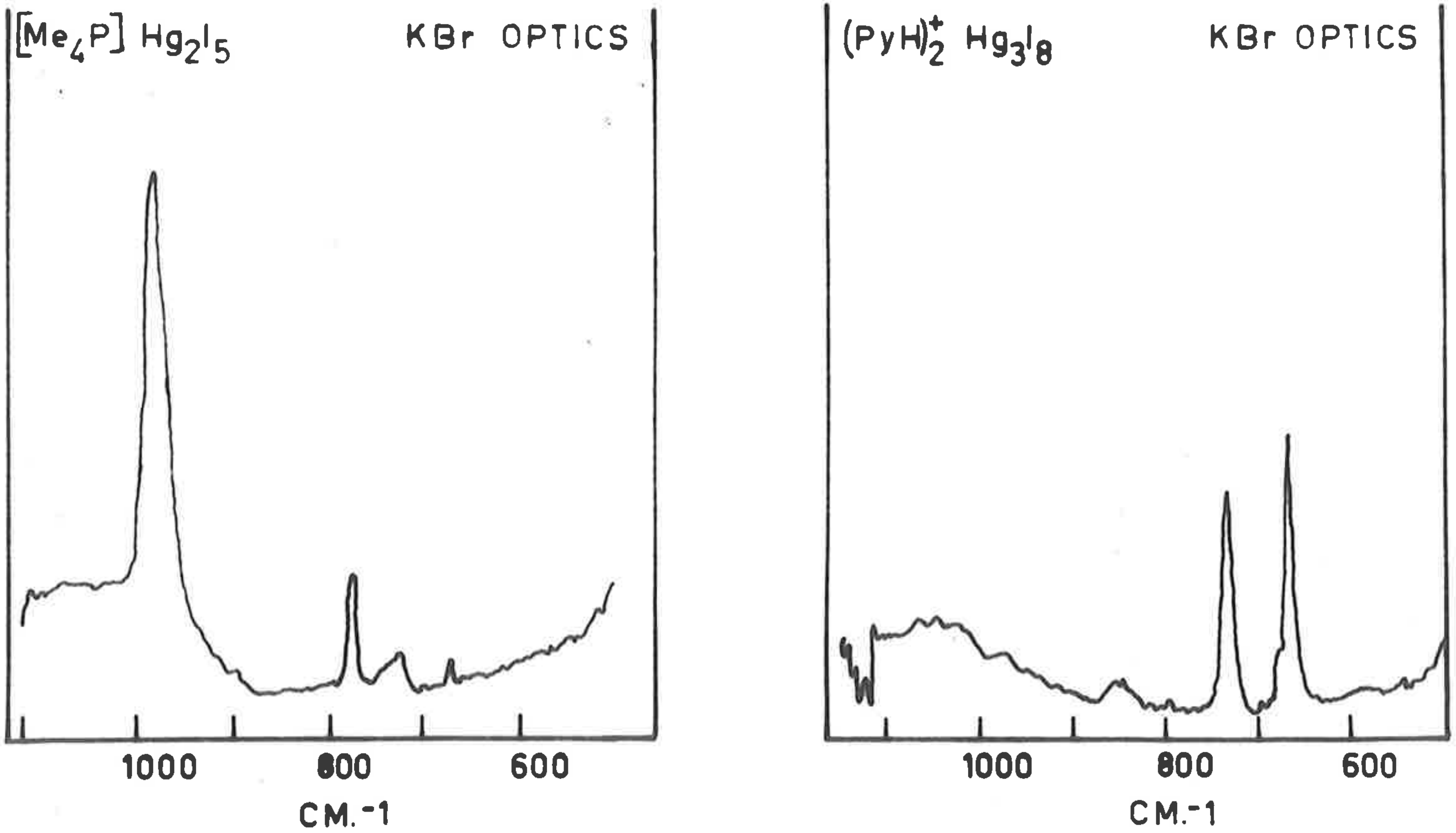

[Me4P] Hg2I5
NaCl OPTICS
N
N
6·5
7·5
6
8
10
12
14
μ
[PyH]2 Hg3I8
NaCl OPTICS
N
N
6·5
7·5
6
8
10 μ
12
14

Fig. 2.4



$[Me_4P]\ Hg_2I_5$
KBr OPTICS
1000
800
600
CM.$^{-1}$
$(PyH)_2^+\ Hg_3I_8$
KBr OPTICS
1000
800
600
CM.$^{-1}$

Fig. 2.5

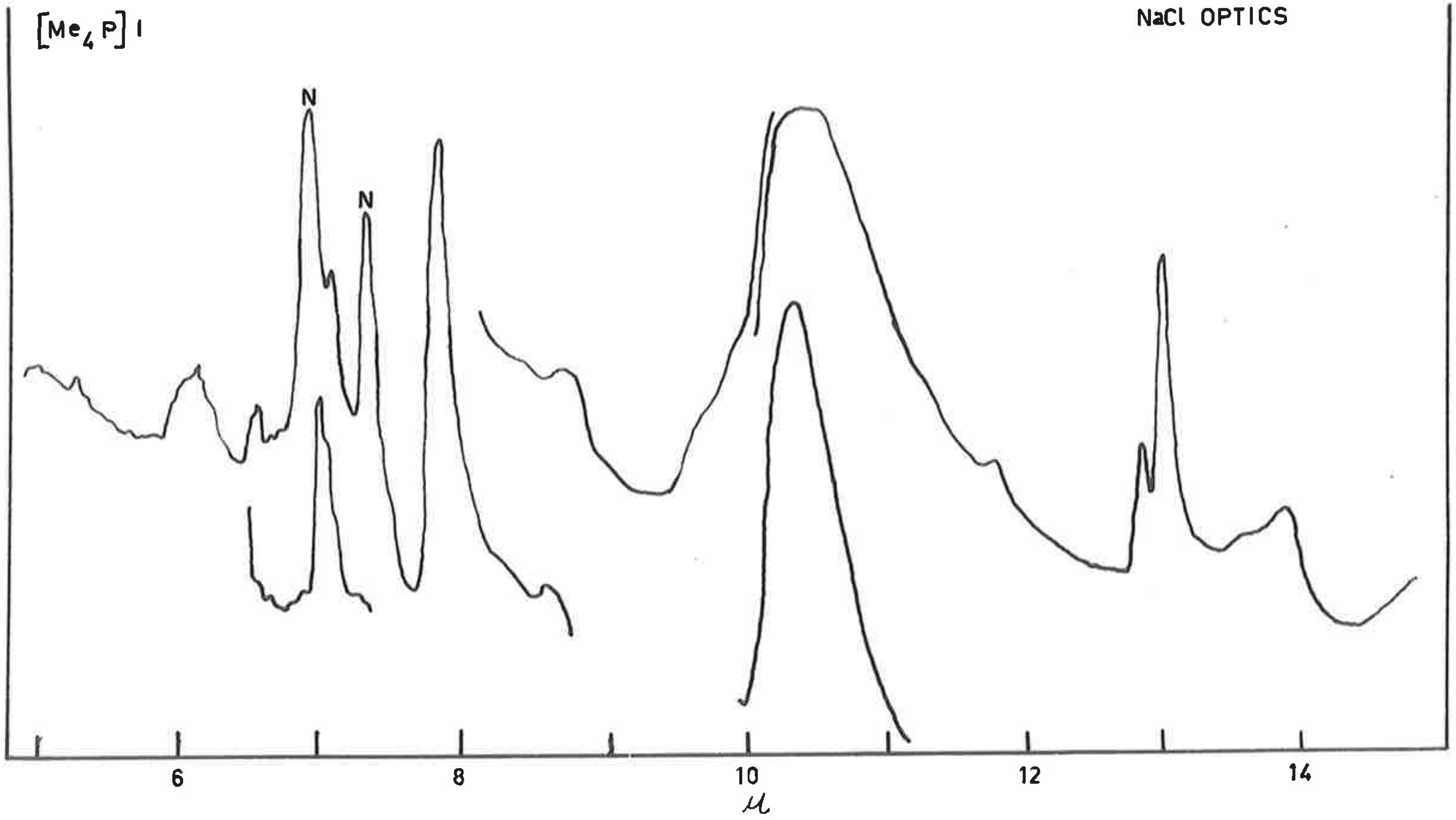


TABLE 2.2

The Principal Infra-red Absorption Bands of Tetramethylphosphonium Compounds and of Trimethylphosphine

[Me$_4$P]I (a) Maxima (Intensity) cm^{-1}	[Me$_4$P]$_2$[HgI$_4$] (a) Maxima (Intensity) cm^{-1}	[Me$_4$P]$_2$[HgI$_4$ (b) Maxima (Intensity) cm^{-1}
1427 (s)	1410 (s)	981 (vs)
1276 (vs)	1393 (s?)	867 (w)
1160 (w)	1325 (w)	777 (s)
971 (vs)	1294 (vs)	740 (w)
850 (w)	862 (w)	724 (w)
780 (m)	773 (s)	
771 (vs)	738 (w)	
719 (w)	722 (w)	
	974 (vs)	

[Me$_4$P][HgI$_3$] (a)	[Me$_4$P][HgI$_3$] (b)	[Me$_4$P][Hg$_2$I$_5$] (a)
1433 (m)	980 (vs)	1433 (m)
1412 (w)	777 (m)	1325 (w)
1300 (m)	724 (w)	1299 (s)
978 (s)		976 (vs)
775 (m)		772 (m)

[Me$_4$P][Hg$_2$I$_5$] (b)	Me$_3$P[9] (a)
980 (vs)	2967 (s)
774 (m)	2899 (s)
724 (w)	1443 (s)
	1431 (s)
	ca. 1280 (m)
	948 (vs)
	938 (vs)
	714 (vs)
	704 (vs)

(a) Sodium chloride optics; (b) potassium bromide optics.

Intensities. (w) weak, (m) medium, (s) strong, (vs) very strong. These are approximate, as the compounds were examined as mulls.

and extremely low lying deformation bands.[11] Thus the observed bands of the tetramethylphosphonium iodomercurates in the 500–2000 cm^{-1} region may be attributed to vibrations associated with the tetramethylphosphonium cation. This is confirmed by the observation that the maxima of bis(pyridinium) octaiodotrimercurate(II) do not correspond to those of the tetramethylphosphonium iodomercurates.

Assignments of the Fundamental Vibrations.

The assignments of the fundamental vibrations of the tetramethylphosphonium compounds and the corresponding vibrations of trimethylphosphine are given in Table 2.3, and those of related compounds are given in Table 2.4. The C-H stretching vibrations of the tetramethylphosphonium compounds which should give bands at ca. 3000 cm^{-1} have not been studied. The spectrum of trimethylphosphine has a doublet near this frequency (Table 2.2), which may be attributed to C-H stretching.

As the maxima of tetramethylphosphonium iodide and its iodomercurate derivatives correspond closely, the vibrational assignments are essentially the same for all these compounds and need not be discussed separately. It may also be concluded that the structure of the cation is not markedly affected by the conversion of the iodide anion to its iodomercurate derivatives.

The assignments for tetramethylphosphonium iodide and its iodomercurate derivatives are largely based on the assignments given for trimethylphosphine oxide[19] and dimethylphosphine.[20] Some assignments have previously been made for trimethylphosphine on the basis of Raman measurements.[14,21] Because of the high symmetry of the tetramethylphosphonium cation, some of its vibrational degrees of freedom are infra-red inactive.

TABLE 2.3

Probable Assignments of Some Fundamental Vibrations of Tetramethylphosphonium Iodide, Tetramethylphosphonium Iodomercurates, and Trimethylphosphine.

Description			Compound		
	Me_3P cm^{-1}	QI cm^{-1}	Q_2HgI_4 cm^{-1}	$QHgI_3$ cm^{-1}	QHg_2I_5 cm^{-1}
Skeletal					
P-C stretch (asym.)	704(vs) 714(vs)	771(vs) 780(m)	773(s)	775(m)	772(m)
Methyl vibrations					
C-H bend (asym.)	1443(s) 1431(s)	1427(s)	1410(s) 1393(s?)	1433(m) 1412(w)	1433(m)
C-H bend (?)			1325(w)		
C-H bend (sym.)	ca.1280(m)	1276(vs)	1294(vs)	1300(m)*	1299(s)
CH_3 rock	948(vs) 938(vs)	971(vs)	974(vs)	978(s)*	976(vs)
CH_3 wag (?)	ca. 830(w)	850(w)	862(w)		

The above maxima are those obtained using NaCl optics.

Q = Me_4P. Abbreviations for intensities as in Table 2.2.

* These intensities were obtained using a low concentration of the complex in Nujol and probably should be (s) and (vs) respectively.

TABLE 2.4

Vibrational Assignments for Compounds Related to the Tetramethylphosphonium Salts.*

Description	Compound Me_4C^a	Me_4Si^b	$[Me_4N]I^c$	Me_3PO^d	Me_2PH^e
Skeletal					
C-M stretch (asym.)	1256(s)	694(vs)	1294(m)	750(s)	704(s) 714(s)
C-M stretch (sym.)	733(R)	598(R)	752(R)	671(R)	615(w)
Methyl vibrations					
C-H bend (asym.)	1475(s)	1430(s)	1483(s)	1420 (ms) 1437 (ms)	1430-1448 (sb) 1445(w)
C-H bend (sym.)	1372(s)	1254(s)	1443(s) 1397(s)	1292(s) 1305(s) 1340(w)	1304(w) 1284(m)
CH_3 rock	925(w)	869(s)	946(vs)	950(s) 872(s)	960(s) 942(s)
CH_3 wag				866(s)	825(vw)

* C-H stretching vibrations are not given, as the corresponding region was not investigated for the tetramethylphosphonium compounds. There is some disagreement over the assignments for the first three compounds (see text).

Abbreviations Intensities: (s) strong, (m) medium, (w) weak, (b) broad, (v) very; combinations of these also used.

The intensities are not strictly comparable as the compounds were not studied in the same state.

M is C, Si, N, P, P respectively.

(R) vibration Raman active only, or only detected by Raman measurements.

References: (a) 12-17; (b) 12-17; (c) 13, 14, 18; (d) 19; (e) 20.

The C-H bending vibration (asym) of trimethylphosphine oxide and dimethylphosphine gives bands in the region 1410-1450 cm^{-1}. The bands of the tetramethylphosphonium compounds in the 1390-1440 cm^{-1} region, and the trimethylphosphine doublet at 1431, 1443 cm^{-1} are considered due to this mode. The methyl deformation in the 1280-1320 cm^{-1} region is considered to be the only reliable correlation band for the P-CH_3 bond,[22] and is caused by a symmetric bending vibration of the C-H bonds.[19,20] A strong or medium intensity band is found in the spectra of all the tetramethylphosphonium compounds and trimethylphosphine in approximately this region. There is a weak band at 1325 cm^{-1} in the spectrum of the tetraiodomercurate complex. A corresponding band has been found for trimethylphosphine oxide at 1340 cm^{-1} and has been attributed to a C-H bending mode.[19] Methyl rocking vibrations of trimethylphosphine oxide occur at 950 cm^{-1} and 872 cm^{-1}, and of dimethylphosphine at 942 cm^{-1} and 960 cm^{-1}. This may be related to the 938, 948 cm^{-1} doublet of trimethylphosphine in the infra-red, and to the Raman line at 948 cm^{-1}. The band shown by the tetramethylphosphonium compounds in the 970-980 cm^{-1} region is probably due to a methyl rocking vibration. The weak band shown by tetramethylphosphonium iodide and the tetraiodomercurate complex at ca. 850 cm^{-1} may possibly be caused by a methyl wagging vibration, which is considered to give bands in the 800-900 cm^{-1} region in the spectra of trimethylphosphine oxide and dimethylphosphine. The remaining strong band of the tetramethylphosphonium compounds, viz., in the 770-780 cm^{-1} region, must be attributed to the P-C asymmetric stretching vibration. This mode gives rise to the 750 cm^{-1} band of trimethylphosphine oxide, the 704, 714 cm^{-1} doublet of dimethylphosphine, and the 710 cm^{-1} Raman line of trimethylphosphine. It follows that the doublet at 704, 714 cm^{-1} in the infra-red spectrum of trimethylphosphine must be assigned to this mode.

These assignments are consistent with those given for tetramethylmethane, tetramethylsilane, and tetramethylammonium iodide (Table 2.4). There has been some argument, however, as to the assignments of the methyl rocking mode and the C-C stretching frequency (asym.) of tetramethylmethane.[12-17] However, the recent work of Shimizu and Murata[12] favours the assignments given in Table 2.4. The assignments of some of the bands of tetramethylammonium iodide[18] were made by analogy with the corresponding bands of tetramethylmethane.[12] The intensities obtained for the maxima of tetramethylphosphonium iodide are similar to those obtained for the corresponding maxima of tetramethylammonium iodide. The marked shift in the M-C (where M is N or P) asymmetric stretching frequency from tetramethylammonium iodide to tetramethylphosphonium iodide is expected as the corresponding frequencies of tetramethylmethane and tetramethylsilane show a similar relationship. A similar shift is found from trimethylamine to trimethylphosphine. The doublet at <u>ca</u>. 1040 cm^{-1} in the infra-red spectrum of trimethylamine[23] may be attributed to the asymmetric N-C stretching vibration, as the corresponding Raman line at 1036 cm^{-1} has been attributed to this mode.[21] The P-C asymmetric vibration of trimethylphosphine gives a doublet at 704, 714 cm^{-1}.

There is one unexpected feature in the spectra of the tetramethylphosphonium compounds. In the Group IVB tetramethyls, the methyl rocking vibration moves to lower energies in the sequence C ⟶ Pb.[13]

From tetramethylammonium to tetramethylphosphonium iodide, however, the methyl rocking vibration moves to a higher energy (946 cm^{-1} to ca. 970 cm^{-1}). The methyl rocking vibration may be assigned to bands at 931 cm^{-1} and 866 cm^{-1} in the spectra of tetramethylarsonium iodide and tetramethylstibonium iodide respectively.[9] These lie in the expected sequence though the frequency of the arsenic compound does not differ markedly from that of tetramethylammonium iodide. It is difficult to explain this unexpected relationship between the ammonium and phosphonium compounds by any property of the free ions. It may be tentatively attributed to some property of the crystalline states of the compounds.

The M-C (where M is N or P) stretching frequency moves to higher energies from trimethylamine and -phosphine to the corresponding tetramethyl compounds. This may possibly be related to the loss of flexibility that must accompany the formation of the fourth M-C bond.

The infra-red spectrum of trimethylphosphine shows more bands[9] than given in Table 2.2. These have not been discussed as they are less intense than the principal bands given, and as corresponding bands are not present in the spectra of the tetramethylphosphonium compounds.

4. Aqueous Decomposition Reactions.[1]

Tetramethylammonium, tetramethylphosphonium, pyridinium, and triphenylmethylarsonium iodomercurates are insoluble in cold water, and only slightly soluble in hot water.* With the exception of triphenyl-

---

* With the possible exception of $[PyH][HgI_3]$ and $[PyH]_2[Hg_3I_8]$, see Chapter 5, section 5.2.

methylarsonium tri-iodomercurate(II), the complexes decompose when heated in aqueous suspension to give either quaternary iodomercurates with a lower iodine to mercury ratio, or mercuric iodide, and a water soluble quaternary iodide. The reactions form a stepwise pattern and are summarized in Table 2.5. Triphenylmethylarsonium tri-iodomercurate(II) does not decompose even on prolonged heating.

The stepwise decomposition of the tetraiodomercurate complex of a particular cation to mercuric iodide proceeds through all the intermediate complexes that can be prepared for that cation. Thus the decomposition of the tetramethylammonium and tetramethylphosphonium tetraiodomercurate complexes proceeds through the tri-iodomercurate and pentaiododimercurate complexes, whereas the decomposition of bis(pyridinium) tetraiodomercurate(II) proceeds through the tri-iodomercurate and octaiodotrimercurate complexes. The failure of triphenylmethylarsonium tri-iodomercurate(II) to react may be related to the inability of the cation to form either a pentaiododimercurate or an octaiodotrimercurate complex, and to the difficulty of solvating the large triphenylmethylarsonium cation. Iodide ions liberated in a particular step inhibit further decomposition. Thus the product of each step may be isolated. An excess of added iodide reverses the reactions. Thus when tetramethylphosphonium tri-iodomercurate(II) is heated with an excess of aqueous potassium iodide, the tetraiodomercurate is obtained.

For a given cation, decomposition of the tetraiodomercurate complex proceeds most readily. The reactions proceed with increasing difficulty as the iodine to mercury ratio of the reacting complex decreases. Of the tetraiodomercurate complexes, decomposition of the

TABLE 2.5

Summary of Aqueous Decomposition Reactions of Quaternary Iodomercurates

(1) $Q_2[HgI_4]_{(s)} \xrightarrow{\text{water}} Q[HgI_3]_{(s)} + Q^+ + I^-$

Q is Me_4N, Me_4P, PyH, Ph_3AsMe.

(2) $2Q[HgI_3]_{(s)} \xrightarrow{\text{water}} Q[Hg_2I_5]_{(s)} + Q^+ + I^-$

Q is Me_4N, Me_4P.

(3) $3Q[HgI_3]_{(s)} \xrightarrow{\text{water}} Q_2[Hg_3I_8]_{(s)} + Q^+ + I^-$

Q is PyH.

(4) $Q[Hg_2I_5]_{(s)} \xrightarrow{\text{water}} 2HgI_{2(s)} + Q^+ + I^-$

Q is Me_4N, Me_4P.

(5) $Q_2[Hg_3I_8]_{(s)} \xrightarrow{\text{water}} 3HgI_{2(s)} + 2Q^+ + 2I^-$

Q is PyH.

s = solid.

tetramethylammonium and tetramethylphosphonium compounds proceeds most readily.

The aqueous decomposition of a single crystal of bis(tetramethylphosphonium) tetraiodomercurate(II) has been examined using a microscope. The single crystal was converted to a polycrystalline aggregate, which retained the shape of the original crystal. There was no obvious crystallographic relationship between the reactant and the product. Further comments on these reactions will be made after possible structures for the iodomercurate complexes have been considered.

In contrast to the behaviour of pyridinium iodomercurates, bis(pyridinium) tetraiodocadmate(II) dissolves on heating with water and can be recovered unchanged.

5. Possible Structures of Crystalline Quaternary Iodomercurate(II) Complexes.

The structures of crystalline quaternary iodomercurate(II) complexes have not been investigated. Since the electronic spectra of the species HgI_4^{2-}, HgI_3^{-}, and HgI_2 in solution are now established (Chapter 3), the visible and ultra-violet reflection spectra of the crystalline iodomercurate complexes should indicate whether such species are present in the crystalline state of these complexes. This technique has been used successfully in studies of complexes of the type $Q[Ph_3P.NiX_3]$ (where Q is a quaternary cation, and X is Br or I).[24] Although facilities for such measurements have not been available, certain qualitative conclusions may be drawn from a comparison of the maxima of the above iodomercurate species in solution and the colours of the solid quaternary iodomercurate complexes. The relevant data are given in Table 2.6. Mercuric iodide has a different structure

TABLE 2.6

Colours of Crystalline Iodomercurate(II) Complexes, and Absorption Maxima of the Electronic Spectra of Iodomercurate Species in Solution

	Complex	Colour	Solution Species	Maxima (A)*
1.	Q_2HgI_4	cream	HgI_4^{2-}	3200-3350; 2650-2730
2.	$QHgI_3$	lemon-yellow	HgI_3^-	3000-3060; 2560-2610
3.	$Q_2Hg_3I_8$	bright yellow		
4.	QHg_2I_5	" "		
5.	HgI_2	red	HgI_2	2650-2750; ca. 2200

For nos. 1, 2, 4, Q is Me_4N, Me_4P. These cations absorb in the far ultra-violet, hence colour cannot be due to cation absorption. For 3, Q is PyH, which does not absorb in the visible or near ultra-violet.

* Values of the maxima of these species in a number of solvents lie within these ranges. This information is taken from Chapter 3, and references therein.

in the solid state (Fig. 2.6),[25] and in solution (Chapter 1, p. 22), and as a consequence the colour of the solid does not correspond to the absorption maxima of the solution species. It may be concluded from the data in Table 2.6 that crystals of the tri-iodomercurate complexes do not contain the HgI_3^- ion. In solution this species does not show pronounced absorption at wavelengths greater than 3200 A, yet the crystalline tri-iodomercurate complexes have a definite yellow colour. It is possible, however, that the HgI_4^{2-} ion is present in solid tetraiodomercurate complexes, as the colour of the crystalline complex is not inconsistent with an absorption band in the 3330 A region. It has been shown that the lattice of a similar tetrachlorozincate(II) complex, $[Me_4N]_2[ZnCl_4]$, does contain the $ZnCl_4^{2-}$ ion.[26]

If it is assumed that the crystalline tetraiodomercurate complexes contain discrete HgI_4^{2-} ions packed with the quaternary cations, it is possible that the other quaternary iodomercurates have structures intermediate between this and the structure of red mercuric iodide, in which complete corner linking of HgI_4 tetrahedra occurs. Various ways of realising the HgI_3, Hg_2I_5, and Hg_3I_8 stoichiometries, based on the linking of HgI_4 tetrahedra, are given in Fig. 2.6. These are purely speculative, as there is no evidence available to show which of these, if any, are correct. Structure 2(a) is related to the known structure of $CsCuCl_3$,[27] while 4(b) is related to that found for $(Bu_3^nAs)_2(HgBr_2)_3$.[28] If the structures of these complexes are based on the linking of HgI_4 tetrahedra, then those structures in which corner linking occurs are possibly to be preferred, as corner linking occurs in red mercuric iodide crystals, and corner linking is favoured by Pauling's rules.[29]

Fig. 2.6

Possible Arrangements of Mercury and Iodine Atoms in Quaternary Iodomercurate(II) Complexes, Based on HgI_4 Tetrahedra.

1. Q_2HgI_4: Discrete HgI_4^{2-} ions.

2. $QHgI_3$:
   (a) Infinite linear system of HgI_4 tetrahedra linked at two corners.
   (b) Discrete $Hg_2I_6^{2-}$ ions; two HgI_4 tetrahedra edge linked.

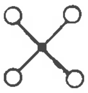
3. QHg_2I_5:
   (a) Infinite linear system, extended in the directions shown. Two HgI_3 chains (structure 2 (a) condensed)
   (b) Infinite linear system, with alternate edge and corner linking of HgI_4 tetrahedra.
   (c) Discrete $Hg_2I_5^-$ ions. Two HgI_4 tetrahedra face linked.
   (d) Infinite system of HgI_4 tetrahedra, extended in the directions shown. Only three corners of each HgI_4 tetrahedron are linked.

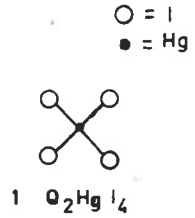
4. $Q_2Hg_3I_8$:
   (a) Infinite linear system extended in the directions shown.
   (b) Infinite linear system. Two HgI_4 tetrahedra edge linked alternating with one corner linked.
   (c) Discrete $Hg_3I_8^{2-}$ ions; three HgI_4 tetrahedra edge linked.
   (d) Analogous to 3 (d). Infinite system with equal numbers of tetrahedra linked at two and three corners.

5. HgI_2 (known structure of the red form):[25]
   Infinite system of HgI_4 tetrahedra, fully corner linked.

Fig. 2.6. Possible Arrangements of Mercury and Iodine Atoms in Quaternary Iodomercurate(II) Complexes, Based on HgI_4 Tetrahedra.

A two dimensional representation of the HgI_4 tetrahedra is used, e.g.





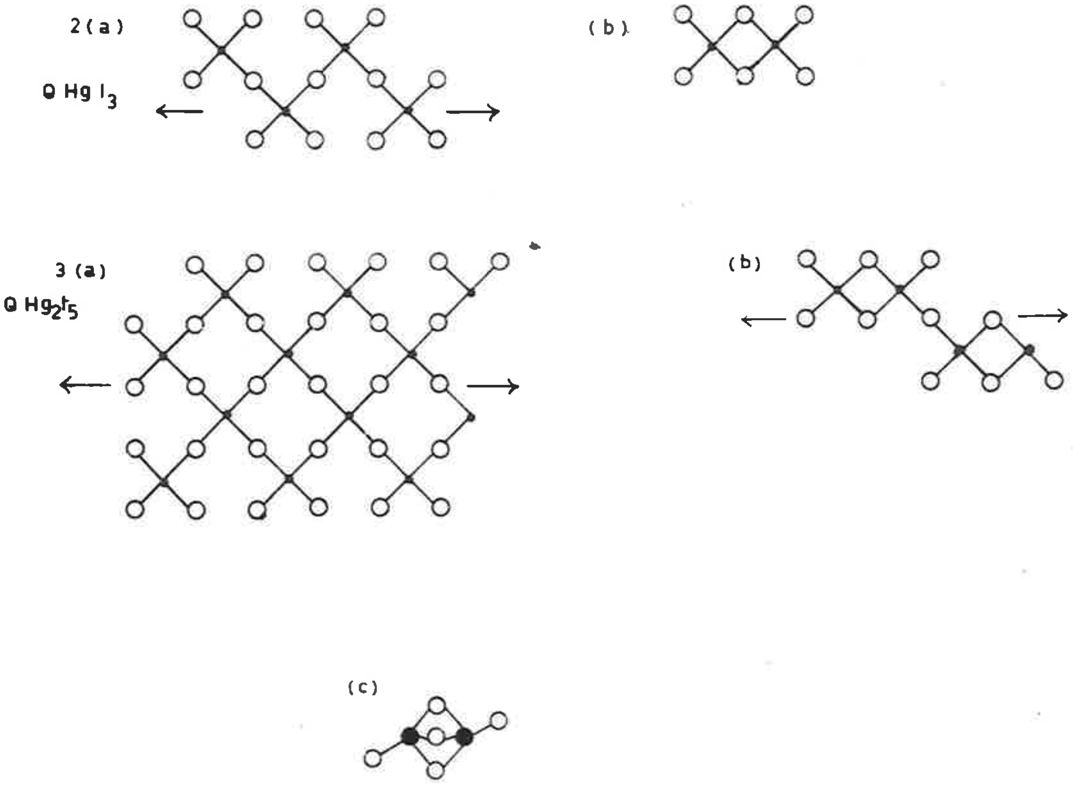
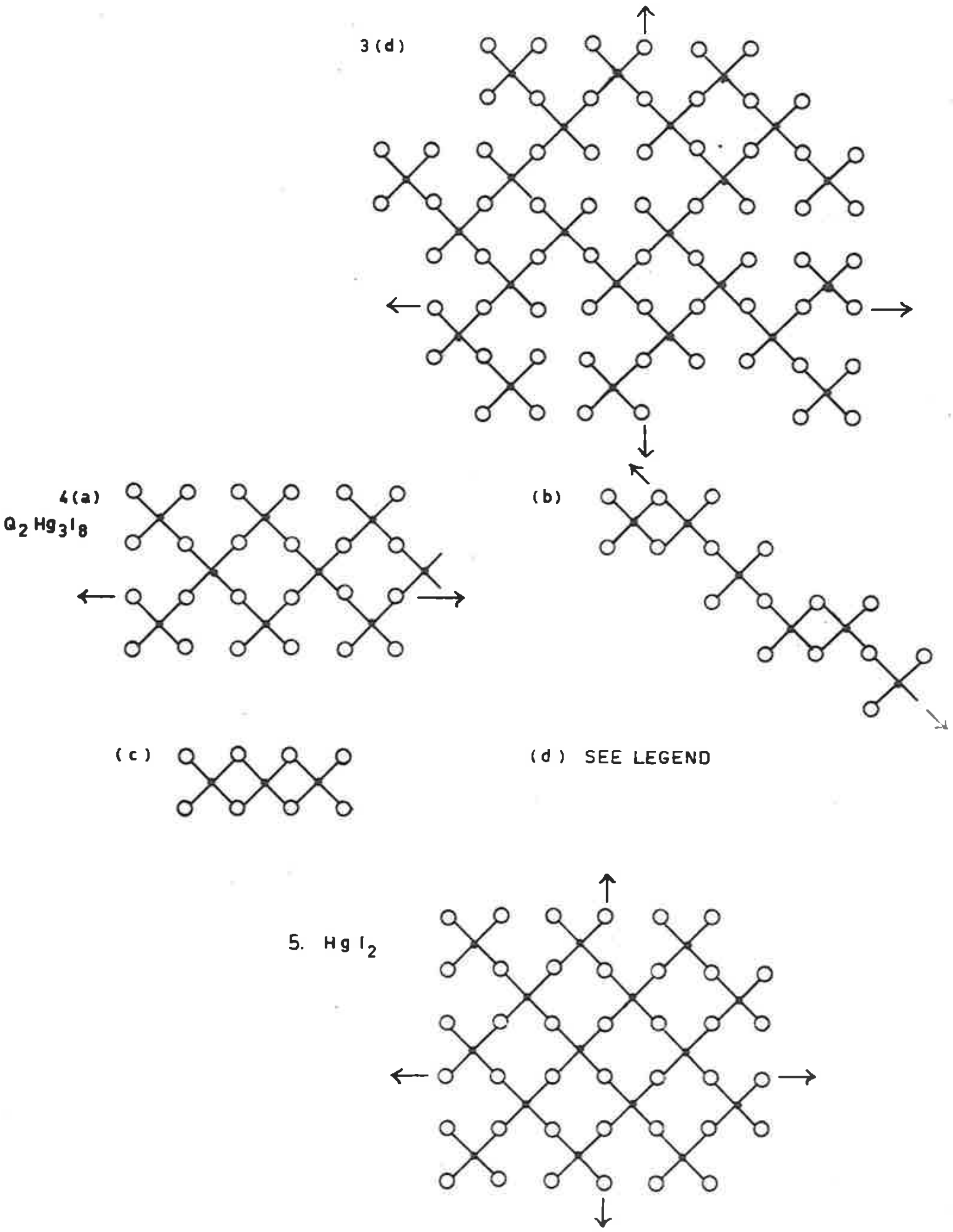


Fig. 2.6 (continued)



Assuming that the structures of crystalline quaternary iodomercurate complexes are based on HgI_4 tetrahedra, the aqueous decomposition reactions can be represented as a stepwise condensation of these tetrahedra from the free HgI_4^{2-} ions to the fully corner linked structure of mercuric iodide. A possible mechanism can also be given for the reactions, e.g., for the tetraiodomercurate ⟶ tri-iodomercurate transition: solvolytic displacement of the quaternary cations in the crystalline tetraiodomercurate might occur, leaving holes into which the HgI_4^{2-} ions could move. They then would condense together, probably by corner linking, with the elimination of iodide ions and an equal number of the displaced quaternary cations. The condensation and elimination would result in the formation of the tri-iodomercurate complex. Successive steps would follow a similar pattern, except that condensation would occur between already linked tetrahedra.

The nature of the decomposition of a single crystal of bis(tetramethylphosphonium) tetraiodomercurate(II) probably supports such a process in preference to a microscopic solution and deposition reaction. The latter would tend to favour random precipitation of the tri-iodomercurate, whereas it was observed that the polycrystalline aggregate of the tri-iodomercurate formed retained the same shape as the original tetraiodomercurate crystal.

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CHAPTER 3

Solution Properties of Group VB Quaternary Iodomercurate(II) Complexes.

1. Ultra-violet Spectra.[1]

The ultra-violet spectra of mercuric iodide and a number of quaternary iodomercurate(II) complexes have been measured in methanol and ethanol from 2300-3200 A. Representative spectra are given in Fig. 3.1 and 3.2, while the positions of the maxima and the corresponding molar* extinction coefficients (ε) are given in Table 3.1.

Mercuric Iodide.

This compound has a single broad band in the region 2300-3200 A in methanol and ethanol. Earlier workers agree that in ethanol the maximum is in the range 2700-2740 A (Chapter 1, Table 1.4).[2-5] There is some disagreement as to the value of $\varepsilon_{max.}$. The values given fall into two groups; one group having values of ca. 5000,[2,3] the other values of ca. 2000.[4,5] The result obtained in this work confirms the higher value for $\varepsilon_{max.}$. The spectrum of mercuric iodide in methanol has been reported,[6] a maximum being found at 2670 A, and $\varepsilon_{max.}$ being 2200. Neither result could be confirmed. In methanol mercuric iodide has a maximum at 2700-2710 A, the value of $\varepsilon_{max.}$ being 5900 (Fig. 3.2, curve 1). Neither the position of the maximum nor the

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* Throughout this chapter molarities of solutions of iodomercurate complexes are expressed in terms of the formula weights of the solid complexes. M is the molarity: C the concentration in gm.ions/litre.

Fig. 3.1. Absorption Spectra in Methanol.

1. $[PMe_4]_2[HgI_4]$, 3.02×10^{-4}M.
2. $[PMe_4][HgI_3]$, 4.00×10^{-4}M, with added $[PMe_4]I$,
   4.00×10^{-4}M.
3. $[PMe_4]_2[HgI_4]$, 2.80×10^{-4}M, with added $[PMe_4]I$,
   21.5×10^{-4}M.
4. $[PMe_4][HgI_3]$ calc.
5. $[PMe_4][HgI_3]$, 4.02×10^{-4}M.
6. $[PMe_4]_2[HgI_4]$, 3.13×10^{-4}M, with added $[PMe_4]I$,
   231×10^{-4} M.

FIG. 3.1. Absorption Spectra in Methanol.

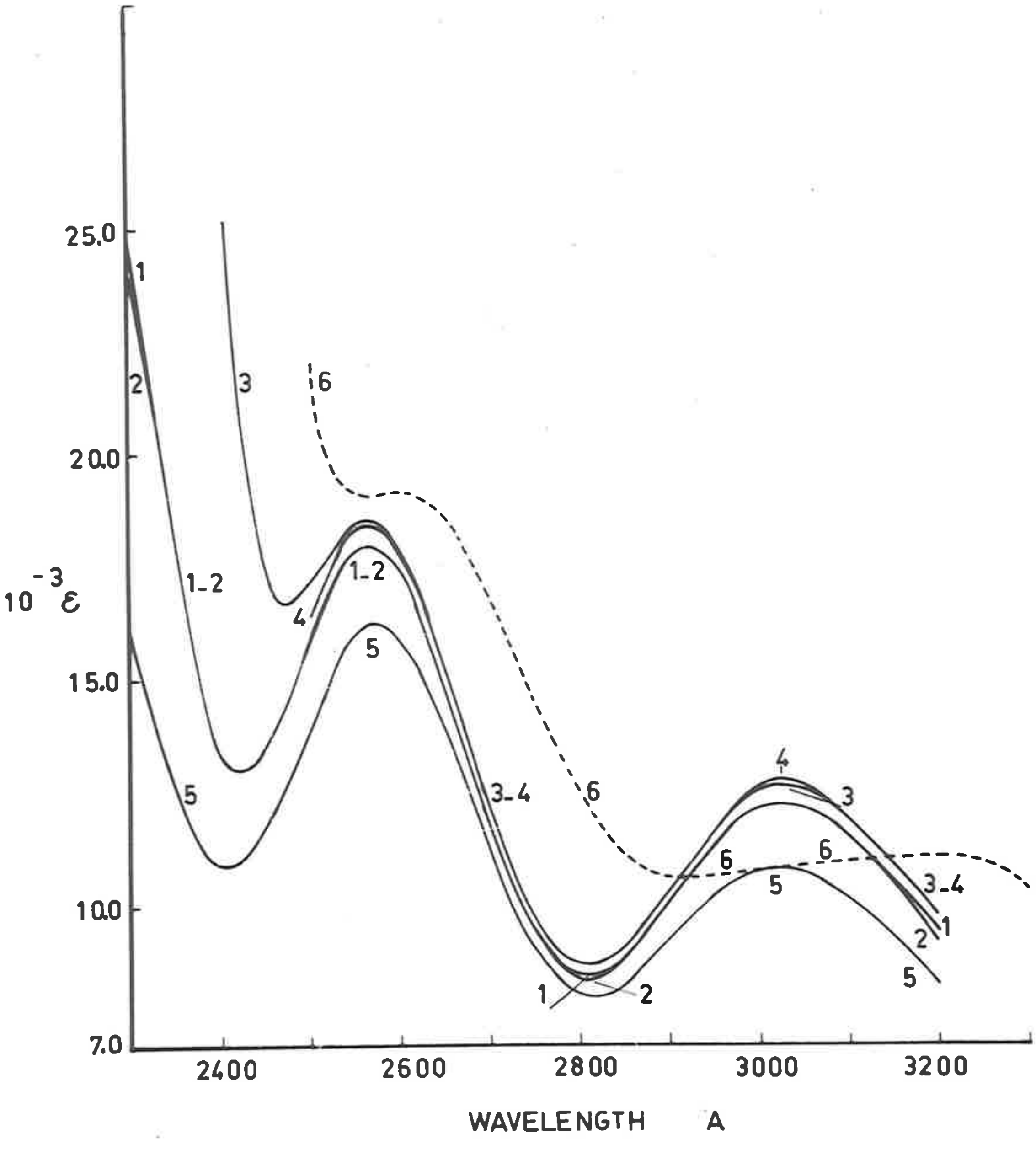

Fig. 3.2. Absorption Spectra in Methanol and Ethanol.

1. HgI_2, 10.9 x 10^{-4}M in methanol.
2. $[PMe_4][HgI_3]$, calc. for methanol.
3. $[PyH][HgI_3]$, calc. for ethanol.
4. $[PMe_4][Hg_2I_5]$, 2.17 x 10^{-4}M in methanol.
5. $[PMe_4][Hg_2I_5]$, calc. for methanol.
6. $[PyH]_2[Hg_3I_8]$, 1.37 x 10^{-4}M in ethanol.
7. $[PyH]_2[Hg_3I_8]$, calc. for ethanol.

FIG. 3.2. Absorption Spectra in Methanol and Ethanol.

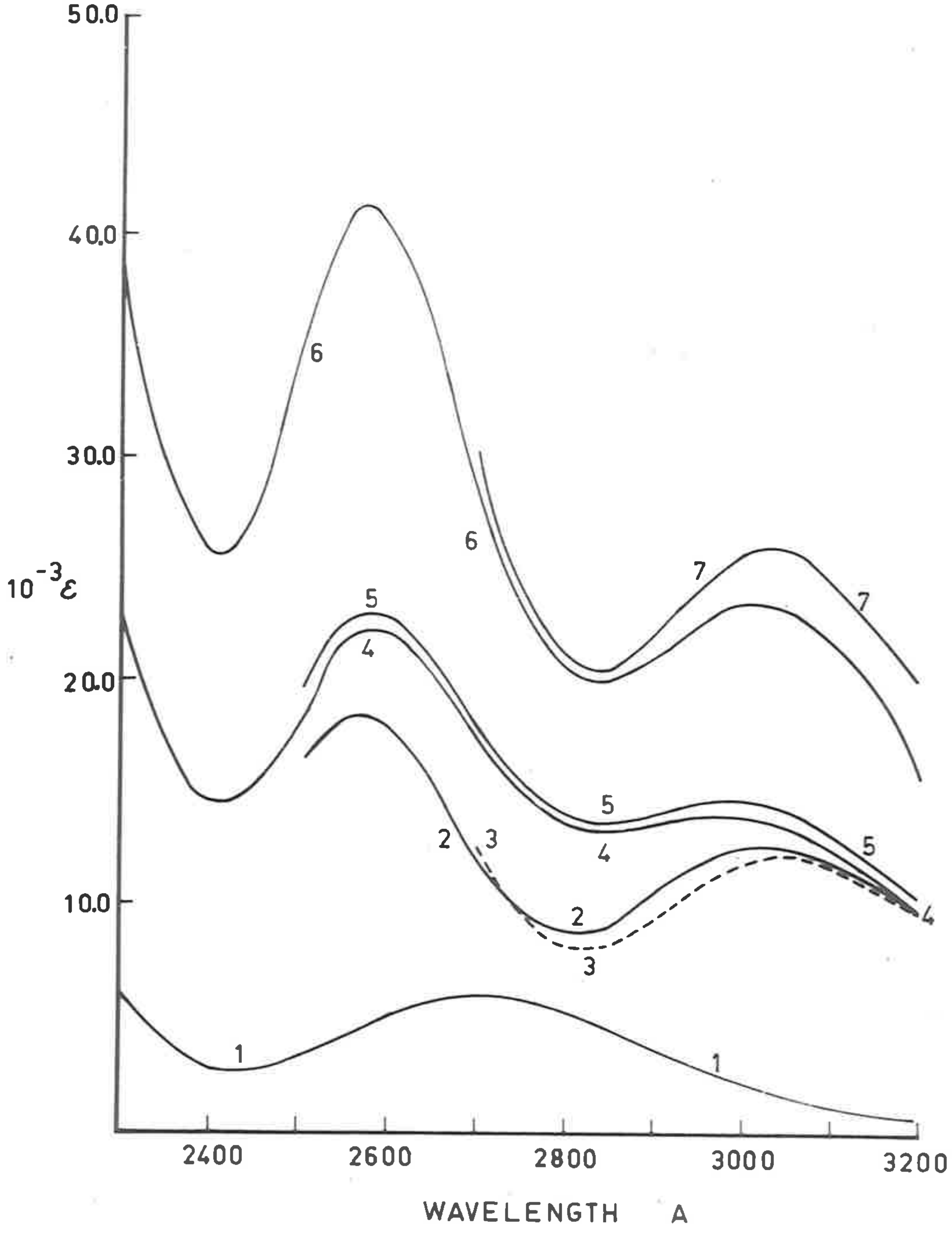

TABLE 3.1

Ultra-violet Absorption Spectra of Quaternary Iodomercurates in Ethanol and Methanol.

	Compound	Concn. 10^4M	Maxima (A) followed by $10^{-3}\epsilon$ in parenthesis	
1.	$[Me_4P]_2[HgI_4]$	2.40	2580(18.1)	3040-3060(12.2)
2.	$[Me_4P][HgI_3]$	3.08	2580-2590(16.3)	3040-3060(11.0)
3.	$[Me_4P][Hg_2I_5]$	2.29	2590-2600(22.6)	3000-3010(14.3)
4.	$[Me_4P]_2[HgI_4]$	1.00	2570-2580(18.7)	3040-3060(12.4)
	$[Me_4P]I$	12.35		
5.	$[PyH]_2[HgI_4]$	2.82	2560-2570(24.8)	3040-3050(12.1)
6.	$[PyH][HgI_3]$	4.15	2570(19.7)	3030-3050(11.0)
7.	$[PyH]_2[Hg_3I_8]$	1.37	2570(41.9)	3010-3030(23.5)
8.	HgI_2	*ca*.0.51	2150(*ca*.24)	2700-2720(*ca*.5.5)
9.	$[Me_4P]_2[HgI_4]$	3.02	2560-2570(18.1)	3010-3030(12.3)
10.	$[Me_4P][HgI_3]$	4.02	2570(16.2)	3020-3030(10.9)
11.	$[Me_4P][Hg_2I_5]$	2.17	2580-2590(22.3)	2960-2990(14.1)
12.	$[Me_4P][HgI_3]$	4.00	2560-2570(18.0)	3010-3040(12.2)
	$[Me_4P]I$	4.00		
13.	$[Me_4P]_2[HgI_4]$	2.80	2560-2570(18.6)	3010-3040(12.6)
	$[Me_4P]I$	21.5		
14.	$[Me_4P]_2[HgI_4]$	3.13	2590-2610(19.2)	3160-3220(11.1)
	$[Me_4P]I$	231	(indistinct)	
15.	HgI_2	10.9		2700(5.9)
		0.85		2700-2710(5.6)
		0.60		2700-2710(5.8)

Nos. 1-8 determined in ethanol at room temperature (*ca*. 20°).
9-13 determined in methanol at 25 ± 0.1°.
14,15 determined in methanol at room temperature.

intensity* at the maximum are changed appreciably on dilution (Table 3.1).

The maximum found for mercuric iodide in methanol and ethanol in the region 2300-3200 A corresponds closely to the maximum found for mercuric iodide vapour, viz., 2660 A [7] or 2680 A.[8] Thus it may be concluded that in methanol and ethanol mercuric iodide exists principally as linear unionized molecules, as in the vapour state.[9]

The Complexes Q_2HgI_4 and $QHgI_3$ (where Q is a quaternary cation.)

(a) In methanol

The spectra of solutions of bis(tetramethylphosphonium) tetraiodomercurate(II) and tetramethylphosphonium tri-iodomercurate(II) in methanol have maxima at the same wavelengths (Table 3.1; Fig. 3.1, curves 1, 5). Thus the solutions must contain the same predominant iodomercurate species at the concentrations studied. The predominant complex must be the tri-iodomercurate ion (HgI_3^-), as it is not possible to account for the intensity of absorption of solutions of the tri-iodomercurate complex by assuming the predominance of the tetraiodomercurate ion. A solution of equimolar amounts of the tri-iodomercurate complex and tetramethylphosphonium iodide has a spectrum identical to that of the tetraiodomercurate complex (Fig. 3.1, curve 2). The addition of a moderate excess of tetramethylphosphonium iodide to a solution of the tetraiodomercurate complex produces no change in the positions of the maxima (Fig. 3.1, curve 3), hence the formation of the tetraiodomercurate ion is negligible. The addition of a large excess of iodide to a solution of the tetraiodomercurate complex does result in the formation of the tetraiodomercurate ion in detectable amounts, as the spectrum is markedly changed (Fig. 3.1, curve 6), the

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* As indicated by the molar extinction coefficients.

higher wavelength maximum being shifted to longer wavelengths (Table 3.1). However, the concentration of the tri-iodomercurate ion is still significant when the molarity ratio of added iodide to the tetraiodomercurate complex is ca. 80:1, as the higher wavelength maximum, though shifted, is not well resolved (Fig. 3.1, curve 6). The lower wavelength maximum is partly masked by iodide absorption (see below).

The difference in intensity of absorption between solutions having the same maxima (Fig. 3.1, curves 1,2,3,5) may be attributed to the equilibrium $HgI_2 + I^- \rightleftharpoons HgI_3^-$, tri-iodomercurate ion formation increasing as the iodide concentration is increased. The equilibrium $HgI_3^- + I^- \rightleftharpoons HgI_4^{2-}$ is unimportant in discussing the spectra of these solutions.

A theoretical spectrum of the undissociated tri-iodomercurate ion in methanol has been calculated for the region 2500-3200 A (Fig. 3.1, curve 4), and corresponds closely to the observed spectrum of a solution of bis(tetramethylphosphonium) tetraiodomercurate(II) containing a moderate excess of iodide (Fig. 3.1, curve 3). The calculations also enable an approximate value of the equilibrium constant for the reaction, $HgI_2 + I^- \rightleftharpoons HgI_3^-$, in methanol at 25°, to be given, viz., 7.5×10^4.

Calculation of the Theoretical Spectrum.

From the foregoing it may be concluded that the observed absorption of solutions of the tetraiodomercurate and tri-iodomercurate complexes at the concentrations studied is due to the absorption of tri-iodomercurate, iodide, and tetramethylphosphonium ions, and mercuric iodide. The spectrum of tetramethylphosphonium iodide in ethanol (and it may be assumed that the behaviour in methanol is very similar) in the region 2300-3200 A resembles that of other ionic iodides, hence the absorption is probably due to iodide ions, and the absorption of the tetramethylphosphonium ions may be neglected. At wavelengths greater than 2500 A, iodide absorption may also be neglected. $\mathcal{E}_{[Me_4P]I}$ is ca. 100 at 2500 A, and decreases further at longer wavelengths (Table 3.2). Thus the observed optical density (D) of solutions of either the tetraiodomercurate or the tri-iodomercurate complex in the region 2500-3200 A is given by the equation

$$D = (\mathcal{E}c)_{HgI_3^-} + (\mathcal{E}c)_{HgI_2} \, {}^*$$

where $c_{HgI_3^-}$ and c_{HgI_2} are equilibrium concentrations. By initially assuming a value of $\mathcal{E}_{HgI_3^-}$ at a particular wavelength, and using the experimental optical densities of solutions of the tri-iodomercurate and tetraiodomercurate complexes and the independently obtained value of $\mathcal{E}_{HgI_2}$ at the same wavelength, the equilibrium composition of the solutions, the equilibrium constant for the reaction, $HgI_2 + I^- \rightleftharpoons HgI_3^-$, at 25° in methanol, and $\mathcal{E}_{HgI_3^-}$ were obtained by a converging series of continuous approximations. The calculations were then repeated at other wavelengths. The data used in the calculations are given in Table 3.2, and the values of $\mathcal{E}_{HgI_3^-}$, the equilibrium constant, and the equilibrium composition of the solutions obtained at different wavelengths are given in Table 3.3. A typical series of continuous approximations are given in Table 3.4.

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* The measured optical densities were suitably corrected for use in this equation which requires values for 1 cm. cells.

TABLE 3.2

Data Used in the Calculation of Theoretical Extinction Coefficients of the Undissociated HgI_3^- Ion

Å	Optical densities (1 mm. cells)					
	D^a	D^b	D^c	D^d	$10^{-3}\varepsilon_{HgI_2}{}^e$	$10^{-3}\varepsilon_{Me_4PI}{}^f$
2500	0.557	0.480			3.2	ca.0.1
2550	0.648	0.540			4.0	
2560	0.652	0.544			4.2	
2570	0.654	0.544			4.4	
2580	0.652	0.541			4.6	
2600	0.636	0.528			5.0	ca.0.03
2700	0.442	0.353	0.473	0.348	5.9	
2720			0.422	0.308		
2800	0.323	0.257	0.309	0.222	5.1	
2810	0.322	0.257			5.0	
2820			0.306	0.220		
2850	0.335	0.271	0.316	0.227	4.3	
2900			0.360	0.262		
2980	0.428	0.362			2.3	
3000	0.433	0.367	0.449	0.330	2.0	
3010	0.435	0.370			1.9	
3020	0.438	0.370			1.8	
3030	0.438	0.370	0.458	0.339	1.7	
3040			0.458	0.340		
3050	0.433	0.367	0.458	0.340	1.5	
3100	0.409	0.349	0.439	0.327	1.0	
3200	0.330	0.283	0.363	0.270	0.5	ca.0.01

(a) $[Me_4P][HgI_3]$ 4.02×10^{-4} M in methanol at 25°.

(b) $[Me_4P]_2[HgI_4]$ 3.02×10^{-4} M in methanol at 25°.

(c) $[PyH][HgI_3]$ 4.15×10^{-4} M in ethanol at *ca.* 20°.

(d) $[PyH]_2[HgI_4]$ 2.82×10^{-4}M in ethanol at *ca.* 20°.

(e) HgI_2 10.9×10^{-4} M in methanol at *ca.* 20°. Values for ε_{HgI_2} in ethanol taken from the data of Fromherz and Lih.[2]

(f) Values for an ethanol solution.

TABLE 3.3

Results of Continuous Approximation Calculations

Wavelength	$10^{-3}\varepsilon_{HgI_3^-}$	10^{-4} K^{a}	Solution Compositions (10^4 M or 10^4 c)			
			$c_{HgI_3^-}$ β	c_{HgI_2} β	$c_{HgI_3^-}$ γ	c_{HgI_2} γ
2500	ca. 16.4	-	-			
2550	18.4	8.3	3.38	0.64	2.91	0.11
2560	18.5_4	8.1	3.37	0.65	2.91	0.11
2570	18.5_0	8.4	3.38	0.64	2.91	0.11
2580	18.4	8.5	3.39	0.63	2.91	0.11
2600	18.0	7.8	3.36	0.66	2.90	0.12
2700	11.9	10.0(?)	3.43	0.59	2.93	0.09
2800	8.7	6.6	3.31	0.71	2.89	0.13
2810	8.7	6.7	3.32	0.70	2.89	0.13
2850	9.2	6.4	3.30	0.72	2.88	0.14
2980	12.4	6.6	3.31	0.71	2.89	0.13
3000	12.6	6.9	3.33	0.69	2.89	0.13
3010	12.7_2	6.7	3.31	0.71	2.89	0.13
3020	12.6_7	7.8	3.36	0.66	2.90	0.12
3030	12.6_5	8.1	3.38	0.64	2.91	0.11
3050	12.6	7.8	3.36	0.66	2.90	0.12
3100	12.0	7.6	3.36	0.66	2.90	0.12
3200	9.7	7.6	3.36	0.66	2.90	0.12

(a) Equilibrium constant for the reaction $HgI_2 + I^- \rightleftharpoons HgI_3^-$ at 25° in methanol: $K_{ave} = 7.5 \times 10^4$ (to the nearest 5×10^3).

(β) Calculated composition of a solution of $[Me_4P][HgI_3]$ 4.02×10^{-4} M.

(γ) Calculated composition of a solution of $[Me_4P]_2[HgI_4]$ 3.02×10^{-4} M. The continuous approximations were carried out using a further significant figure than given above, hence the small difference in equilibrium constants obtained for the same apparent solution compositions.

(?) Probably a significant error in the experimental data used - not included in averaging the values of K.

TABLE 3.4

A Typical Series of Continuous Approximations

Using experimental data for the wavelength 3000 A.

$10^{-3}\varepsilon_{\mathrm{HgI}_3^-}$ [α]	$10^{-4}K$ [β]	Solution compositions (10^4 M or 10^4 G.)				
		$c_{\mathrm{HgI}_3^-}$ [γ]	c_{HgI_2} [γ]	$c_{\mathrm{HgI}_3^-}$ [∂]	c_{HgI_2} [∂]	
12.50	7.66	3.358	0.662	2.903	0.120	
12.56	7.20	3.339	0.681	2.895	0.128	
12.59	7.00	3.330	0.690	2.892	0.131	
12.60	6.91	3.326	0.694	2.891	0.132	
12.6	6.9	3.33	0.69	2.89	0.13	Accepted data

(α) The value 12.50 was assumed initially, while the subsequent values were obtained from the calculations.

(β) Equilibrium constant for the reaction $\mathrm{HgI}_2 + \mathrm{I}^- \rightleftharpoons \mathrm{HgI}_3^-$ at 25° in methanol.

(γ) Calculated composition of a solution of $[\mathrm{Me}_4\mathrm{P}][\mathrm{HgI}_3]$ $4.02_0 \times 10^{-4}$ M in methanol.

(∂) Calculated composition of a solution of $[\mathrm{Me}_4\mathrm{P}]_2[\mathrm{HgI}_4]$ $3.02_3 \times 10^{-4}$ M in methanol.

The calculated extinction coefficients are not very sensitive to small errors in the experimental optical densities, whereas values of the equilibrium constant are markedly affected. This accounts for the variation in the values obtained for the equilibrium constant, viz., $6.4-8.5 \times 10^4$. (The single value 10×10^4 has been rejected.)

The method outlined for the calculation of the spectrum of the tri-iodomercurate ion should be useful in obtaining the spectra of other anionic metal halide complexes, for which data are not available at present, e.g., $HgBr_3^-$, $HgCl_3^-$, and CdI_3^-. It may also be suitable for the study of mixed complexes such as HgI_2Br^- and HgI_2Cl^-. Its suitability in the present simple form depends on there being a significant difference between the stabilities of the various complexes likely to be present, such that the observed absorption can be attributed to two complexes only, linked by a single equilibrium.

(b) In ethanol

The relationship between the spectra of solutions of tetramethylphosphonium tri-iodomercurate(II) and bis(tetramethylphosphonium) tetraiodomercurate(II) in ethanol is the same as in methanol (Table 3.1). The maxima are shifted to slightly longer wavelengths in ethanol, but the values of $\varepsilon_{max.}$ correspond closely to those in methanol. Addition of a moderate excess of iodide to a solution of the tetraiodomercurate in ethanol produces no change in the positions of the maxima (Table 3.1). Similar arguments to those used for the corresponding spectra in methanol show that the tri-iodomercurate ion is the dominant iodomercurate species present in these solutions.

The spectra of bis(pyridinium) tetraiodomercurate(II) and pyridinium tri-iodomercurate(II) in ethanol are similar to those of the corresponding tetramethylphosphonium compounds, but are complicated by pyridinium ion absorption[10] at wavelengths less than 2700 A. The maxima of solutions of these complexes are given in Table 3.1. A theoretical spectrum of the undissociated tri-iodomercurate ion in ethanol has been calculated for the region 2700-3200 A (Fig. 3.2, curve 3), using the reported extinction coefficients of mercuric iodide in ethanol,[2] and the optical densities obtained for solutions of pyridinium tri- and tetraiodomercurates (Table 3.2). As the solutions were not thermostatted for the measurement of the latter spectra, the equilibrium constants obtained varied considerably, but are of the same order, viz., 10^5 as those obtained in methanol.

The variation of optical density with concentration has been studied for solutions of tetramethylphosphonium and pyridinium tri- and tetraiodomercurates in ethanol. A slight departure from Beer's law is found for solutions of each compound in the concentration range ca. $0.07-7.0 \times 10^{-4}$ M, the deviation being greater for solutions of the tri-iodomercurate complexes. These results are illustrated in Fig. 3.3-3.5 for optical densities obtained at 3040 A. At this wavelength cation absorption is negligible, hence the data for the two tetraiodomercurate complexes lie on the same plot (Fig. 3.3). The two tri-iodomercurate complexes show the same behaviour (Fig. 3.4). Expansion of the concentration scale for the more dilute solutions shows the deviation from Beer's law clearly (Fig. 3.5). The straight lines in Fig. 3.5 have been weighted to pass through optical densities for concentrations less than 0.400×10^{-4} M. The peaks become less distinct with dilution, but the positions of the maxima are not appreciably

FIG. 3.3 VARIATION OF OPTICAL DENSITY WITH CONCENTRATION OF IODOMERCURATE COMPLEXES IN ETHANOL

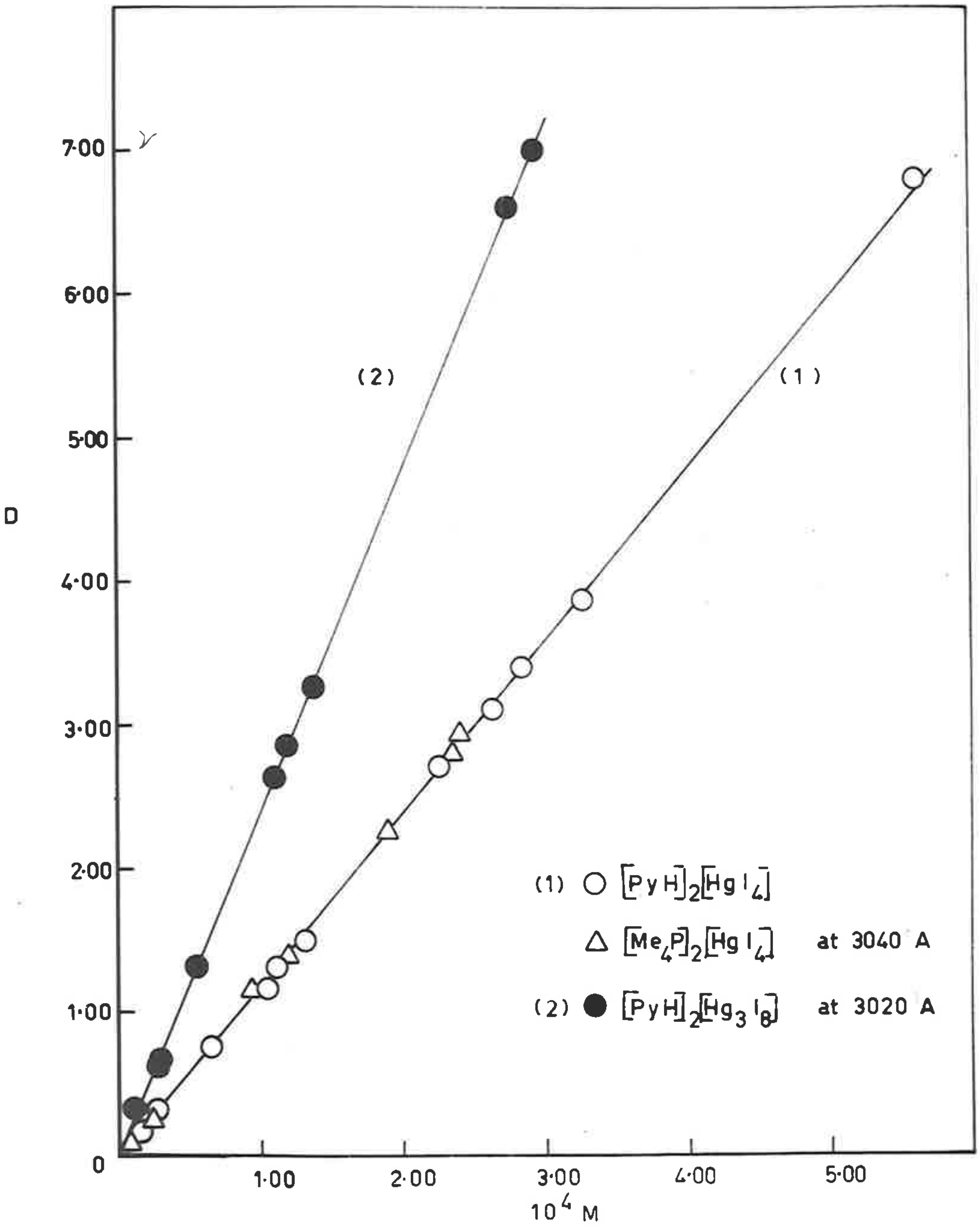


FIG. 3.4 VARIATION OF OPTICAL DENSITY WITH CONCENTRATION OF IODOMERCURATE COMPLEXES IN ETHANOL

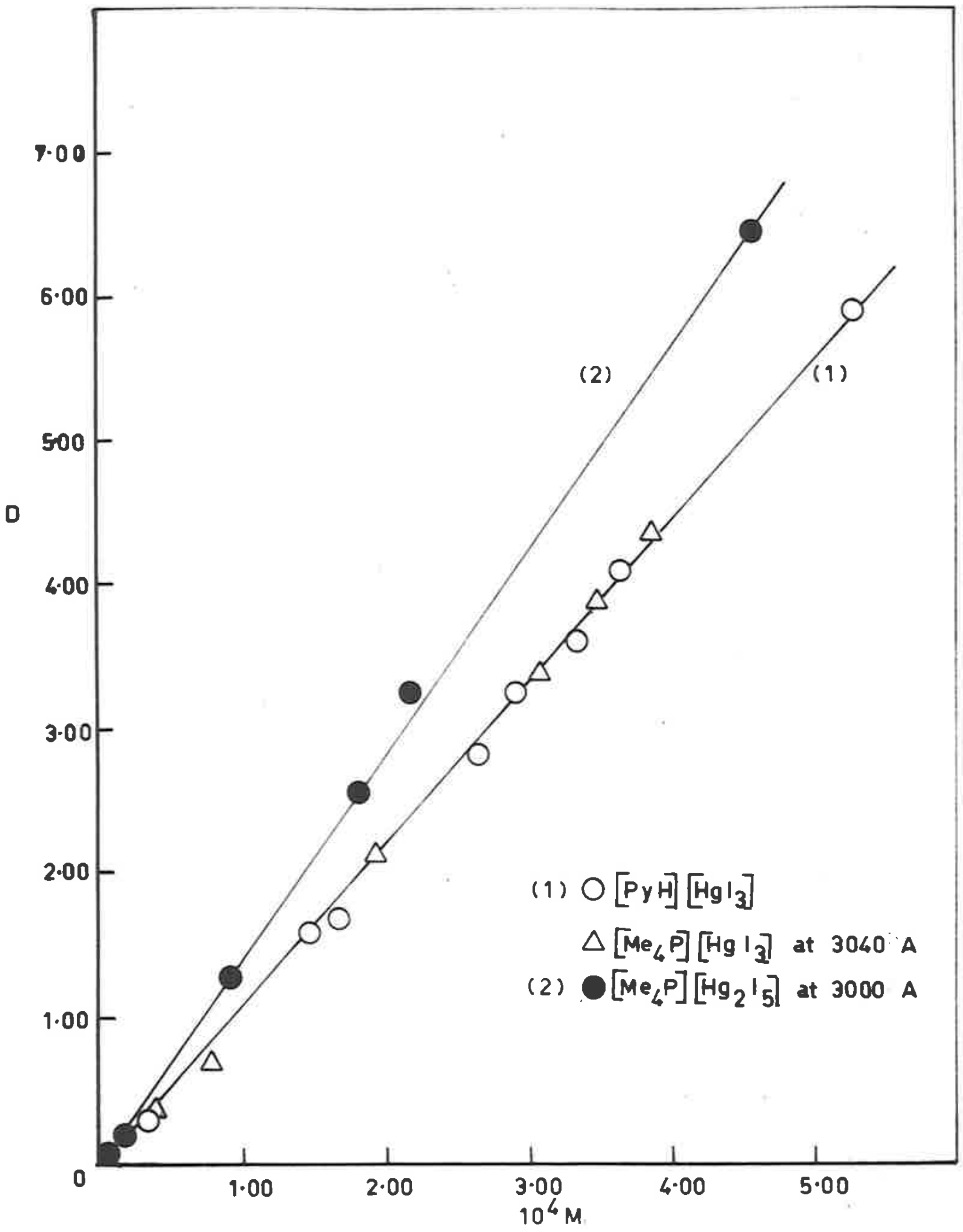
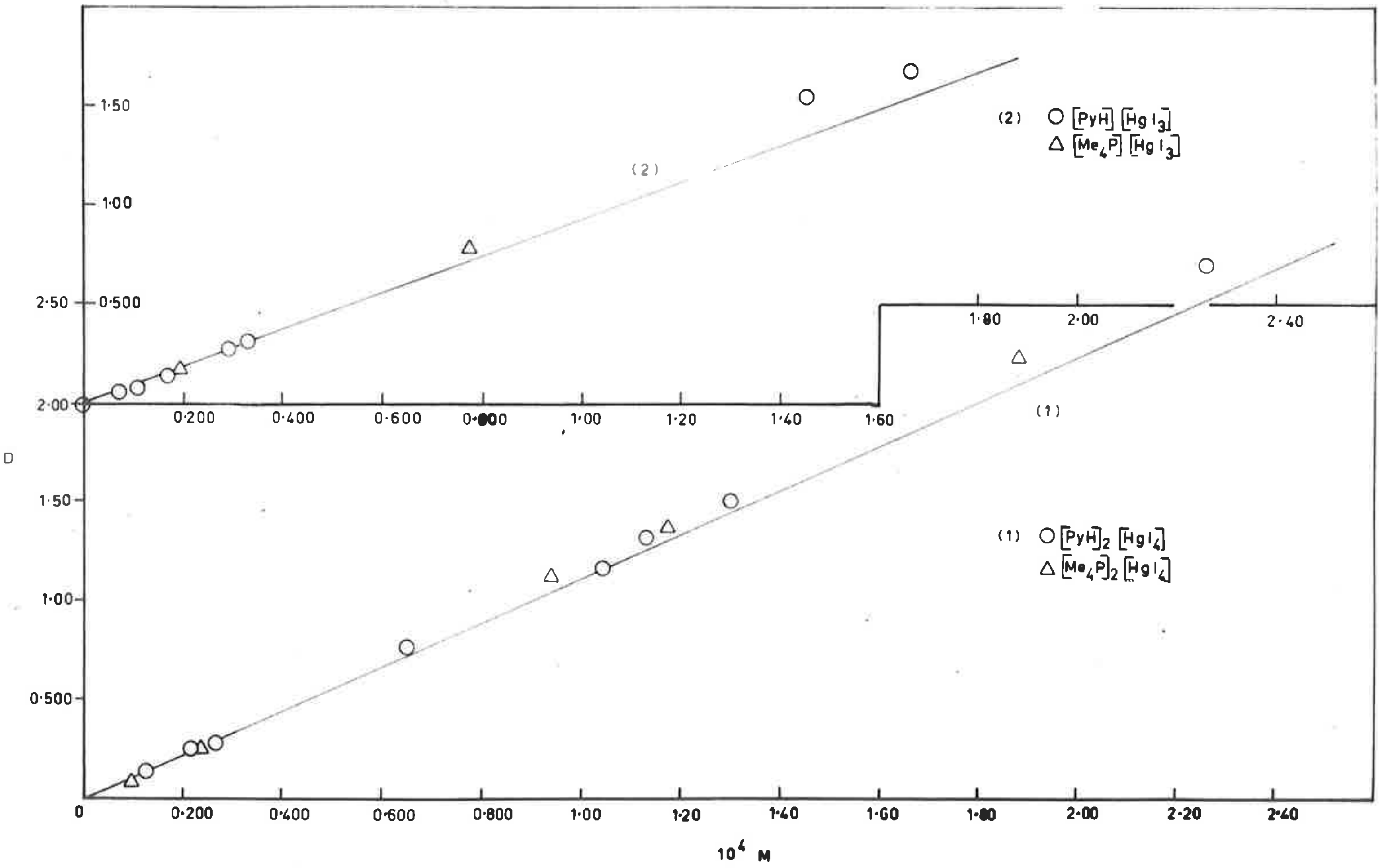


FIG 3.5 VARIATION OF OPTICAL DENSITY WITH CONCENTRATION OF IODOMERCURATE COMPLEXES IN ETHANOL



altered. This behaviour is consistent with the presence of the tri-iodomercurate ion as the dominant iodomercurate species in the solutions in equilibrium with mercuric iodide and iodide ions, the concentration of the tetraiodomercurate ion being negligible.

This interpretation of the ultra-violet spectra is consistent with the earlier results of Fromherz and Lih[2] (Chapter 1, p. 16,17), and with the recent results of Griffiths and Symons.[11] The spectra of mercuric iodide in aqueous and ethanolic solutions of alkali metal iodides[2] show maxima at 2670 A and 3230 A in water, and at 2730 A and 3290 A in ethanol, which have been attributed to the tetraiodomercurate ion. Distinct maxima were only obtained with either very high ratios of MI:HgI_2 (where M is an alkali metal), or by using much higher concentrations than in the present work when MI:HgI_2 was ca. 2:1. This supports the interpretation of the spectral changes on the addition of a large excess of iodide to a solution of bis(tetramethylphosphonium) tetraiodomercurate(II). Griffiths and Symons[11] studied the spectra of mixed solutions of mercuric iodide and tetra-n-butylammonium iodide in acetonitrile, methyl formate, ethyl formate, methylene dichloride, and N,N'-dimethylformamide,* and attributed maxima at 2590-2610 A and 3010-3060 A to the tri-iodomercurate ion. The maxima of the tri-iodomercurate ion in ethanol and methanol occur at comparable wavelengths.

The Complexes QHg_2I_5 and $Q_2Hg_3I_8$ (where Q is a quaternary cation).

The spectrum of tetramethylphosphonium pentaiododimercurate(II)

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* Henceforth termed dimethylformamide in this Chapter.

in methanol (Fig. 3.2, curve 4) is similar to the spectra of the corresponding tri- and tetraiodomercurate complexes in the same solvent. Compared with the theoretical spectrum of the undissociated tri-iodomercurate ion (Fig. 3.2, curve 2), the spectrum of the pentaiododimercurate complex shows only slight shifts in the absorption maxima, but shows enhanced absorption in the region 2500-3000 A, where mercuric iodide has its absorption band (Fig. 3.2, curve 1). It is therefore considered that in solution the pentaiododimercurate complex undergoes dissociation into mercuric iodide and the tri-iodomercurate ion, thus

$$[Me_4P][Hg_2I_5] \longrightarrow Me_4P^+ + HgI_3^- + HgI_2.$$

A theoretical spectrum for tetramethylphosphonium pentaiododimercurate(II) (Fig. 3.2, curve 5) has been constructed assuming this solution composition, using the measured extinction coefficients of mercuric iodide and those calculated for the undissociated tri-iodomercurate ion in methanol, and closely agrees with that obtained experimentally for the pentaiododimercurate complex. The slight differences in intensity between the theoretical and experimental spectra may be explained by partial dissociation of the tri-iodomercurate ion into mercuric iodide and iodide. The value of the equilibrium constant for the reaction $HgI_2 + I^- \rightleftharpoons HgI_3^-$ in methanol indicates that the presence of an equivalent molarity of mercuric iodide is insufficient to prevent some dissociation of the tri-iodomercurate ion at the concentrations used. In ethanol the spectrum of the pentaiododimercurate complex closely resembles that obtained in methanol, (The relevant maxima are given in Table 3.1.) and a similar explanation of its solution chemistry may be given. Ethanol solutions of the complex show good agreement with Beer's law for the concentration range 0.09-3.00 x 10^{-4} M at 3000 A (Fig. 3.4). (Some deviation occurs at the lower concentrations though this is not readily evident from Fig. 3.4.) This would not be expected if significant amounts of the pentaiododimercurate ion were present at the higher concentrations used, however it is readily understood with the foregoing description of the solution composition. The dissociation of the tri-iodomercurate ions, formed by the initial dissociation of the pentaiododimercurate complex, on dilution is inhibited by the mercuric iodide also produced in the initial dissociation.

The spectrum of bis(pyridinium) octaiodotrimercurate(II) (Fig. 3.2, curve 6) in ethanol has a similar shape to the spectra of pyridinium tri- and tetraiodomercurates in the same solvent, the maxima occurring in similar positions (Table 3.1). Similar arguments to those used for the pentaiododimercurate complex show that the octaiodotrimercurate complex undergoes dissociation in solution into tri-iodomercurate ions and mercuric iodide.

$$[PyH]_2[Hg_3I_8] \longrightarrow 2[PyH]^+ + 2HgI_3^- + HgI_2$$

A theoretical spectrum has been constructed for this complex for the wavelength region 2700-3200 A (Fig. 3.2, curve 7) assuming this solution composition, and using the extinction coefficients of mercuric iodide in ethanol[2] and those calculated for the undissociated tri-iodomercurate ion in ethanol. The theoretical spectrum reproduces the shape of the experimental spectrum, but shows greater absorption throughout the wavelength range. This may be explained by partial dissociation of the tri-iodomercurate ions as in the discussion of the pentaiododimercurate complex. As found, this dissociation is expected to be greater for the octaiodotrimercurate complex, as the initial ratio of mercuric iodide to tri-iodomercurate is 1:2 (1:1 in the case of the pentaiododimercurate complex), so that the effect of mercuric iodide in inhibiting dissociation of the tri-iodomercurate ions is smaller in solutions of this complex. Bis(pyridinium) octaiodotrimercurate(II) shows good agreement with Beer's law at 3020 A for the concentration range 0.05-2.75 x 10^{-4} M (Fig. 3.3), (Some deviation occurs at the lower concentrations though this is not readily evident from Fig. 3.3.) and the positions of the maxima are scarcely altered on dilution. This is consistent with the foregoing description of the solution chemistry of the complex.

Stoichiometry of the Solid Complexes and Solution Composition.

These studies of the ultra-violet spectra of iodomercurate complexes show that it is impossible to predict the dominant iodomercurate species present in solutions of iodomercurate complexes on the basis of the solid state stoichiometries, e.g., in methanol and ethanol tetraiodomercurate complexes give tri-iodomercurate ions as the dominant iodomercurate species at the concentrations studied, the concentration of the tetraiodomercurate ions being negligible. The assignments of the ultra-violet absorption bands of iodomercurate complexes in aqueous ethanol given by Gallais[12] were made on this basis, and are thus not necessarily correct. Comparison of these assignments (Table 1.4) with the results of the present study and of other workers[2,11] (Table 1.4) shows that the maxima given for the tetraiodomercurate ion are wrong, but that those given for the $HgI_3.H_2O^-$ ion correspond approximately to those found for the tri-iodomercurate ion, though the corresponding intensities are probably too low.

Origins of the Ultra-violet Spectra.

This topic has been discussed (Chapter 1, p. 18), but some further remarks may now be made. Katsin[13] suggested that halogen atoms are formed during light absorption by a variety of halogen containing compounds. It remains to compare the theoretical splitting between the $^2P_{3/2}$ and the $^2P_{1/2}$ states of the iodine atom with the observed energy separation between the bands of the various iodomercurate complexes. Table 3.5 contains the positions of the maxima of the various iodomercurate species in a number of solvents together with the energy separation between the maxima. The theoretical splitting between the two states of the iodine atom is 7600 cm^{-1},[14] while experimentally it is found that ionic iodides, which should most readily give iodine atoms on light absorption, have band separations of a similar magnitude, e.g., the splitting for aqueous potassium iodide[15] is 7350 ± 14 cm^{-1}. The anionic iodomercurate complexes have maxima corresponding to a splitting of 5000-6500 cm^{-1}, while mercuric iodide has a band separation of 9500-10,000 cm^{-1} in solution. The band separations deviate too far from the theoretical splitting to support the suggestion that iodine atoms are formed during light absorption by these complexes. A description of light absorption similar to that given by Griffiths and Symons[11] for mercuric iodide (Chapter 1, p. 19) is more suitable for all iodomercurate complexes.

2. Conductivity Measurements.[16]

The conductivities of a number of quaternary iodomercurate(II) complexes and related compounds have been measured in acetone. The results are summarised in Fig. 3.6-3.9, in which the variation of the

TABLE 3.5

Positions of Maxima for the Iodomercurate Complexes in Various Solvents, Together with the Energy Separation between the Absorption Bands

The data of Fromherz and Lih,[2] and of Griffiths and Symons,[11] are used, together with the results obtained in this work.

Complexes	Maxima (A) (energy separation in cm^{-1})				
HgI_2	2150^a	2100^b			
	2720	2650			
	(9800)	(9900)			
HgI_3^-	2580^a	2560^c	2605^d	2590^e	2610^f
	3050	3020	3010	3030	3060
	(6000)	(5900)	(5100)	(5300)	(5600)
HgI_4^{2-}	2730^a	2670^b			
	3290	3230			
	(6200)	(6500)			

Solvents: (a) ethanol, (b) water, (c) methanol,
(d) acetonitrile, (e) methyl formate,
(f) ethyl formate, methylene dichloride.

As the higher wavelength band is broad, there is some uncertainty as to the actual position of this maximum. The values given are correct to ± 20 A.

molar conductance with the square root of the molarity is shown. The results have been shown to be reproducible within the limits of error shown in the figures. For the purposes of the present investigation, the relative conductances and not the absolute values of the conductances are important. All measurements have been made using similar conditions and hence are comparable.

The Complexes $QHgI_3$ (where Q is a quaternary cation).

The molar conductance of tetramethylphosphonium tri-iodomercurate(II) in acetone (Fig. 3.6) shows near linear variation with the square root of the molarity in the concentration range 2-13 x 10^{-4}M, but at lower concentrations the conductance rises steeply. This may be attributed to the dissociation of the tri-iodomercurate ion, $HgI_3^- \rightleftharpoons HgI_2 + I^-$, the extent of which increases on dilution. Thus on dilution the observed conductance of the tri-iodomercurate complex increasingly deviates from that expected if no dissociation occurred. The molar conductance of mercuric iodide (Fig. 3.6) is very small at concentrations greater than 1 x 10^{-4} M, but at lower concentrations the conductance rises steeply as does that of tetramethylphosphonium tri-iodomercurate(II) in the same concentration region. The conductance of the other dissociation product, tetramethylphosphonium iodide (Fig. 3.8), exceeds the observed conductance of the tri-iodomercurate complex at concentrations less than 3 x 10^{-4} M. The considerable uncertainty in the values of the conductance of tetramethylphosphonium iodide is due to its low solubility in acetone making it difficult to obtain accurate solutions.

The molar conductance of tetramethylammonium tri-iodomercur-

FIG.3.6 CONDUCTIVITIES OF IODOMERCURATE COMPLEXES AND MERCURIC IODIDE IN ACETONE AT 25°

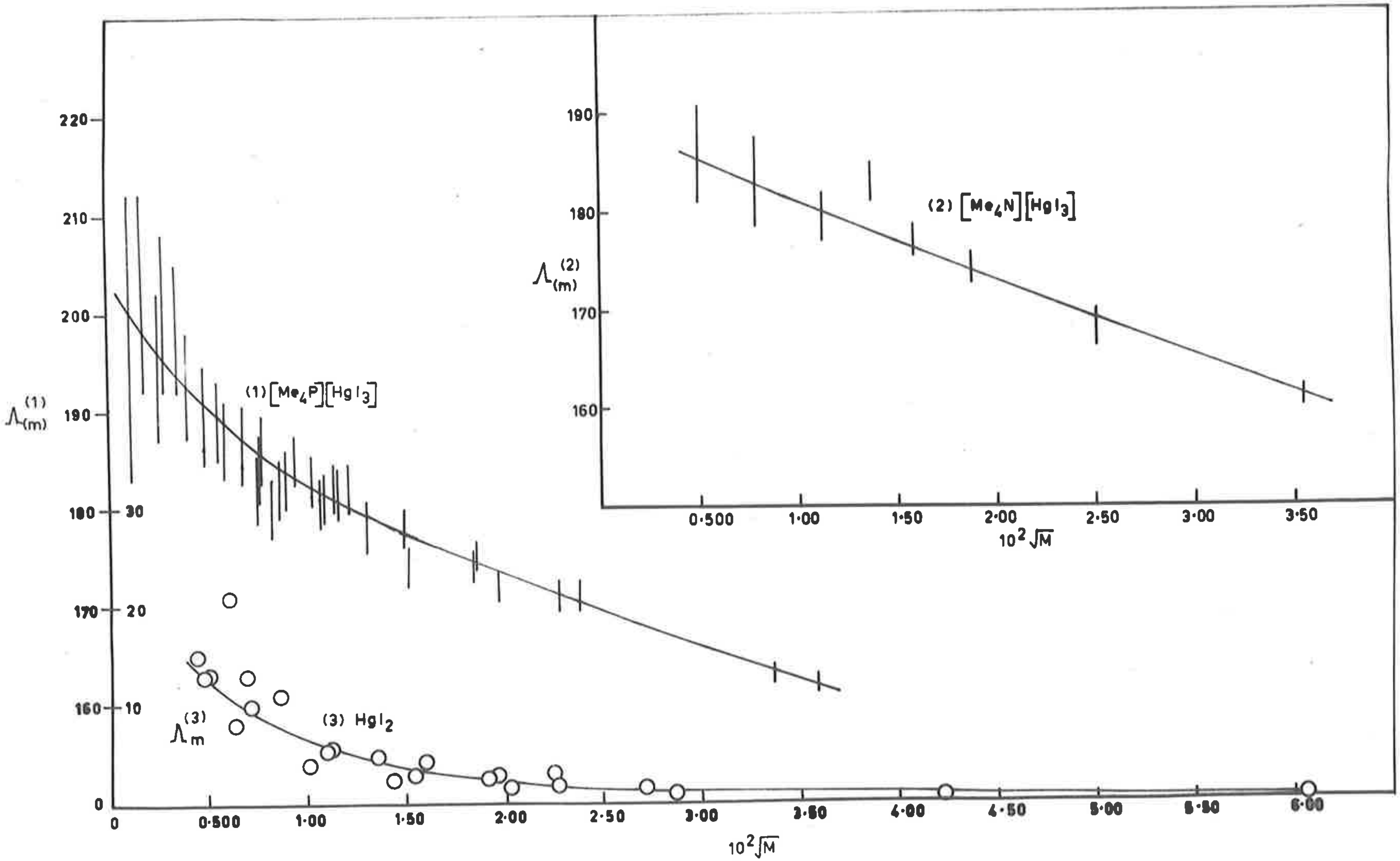


FIG. 3.7 CONDUCTIVITIES OF QUATERNARY IODOMERCURATES IN ACETONE AT 25°

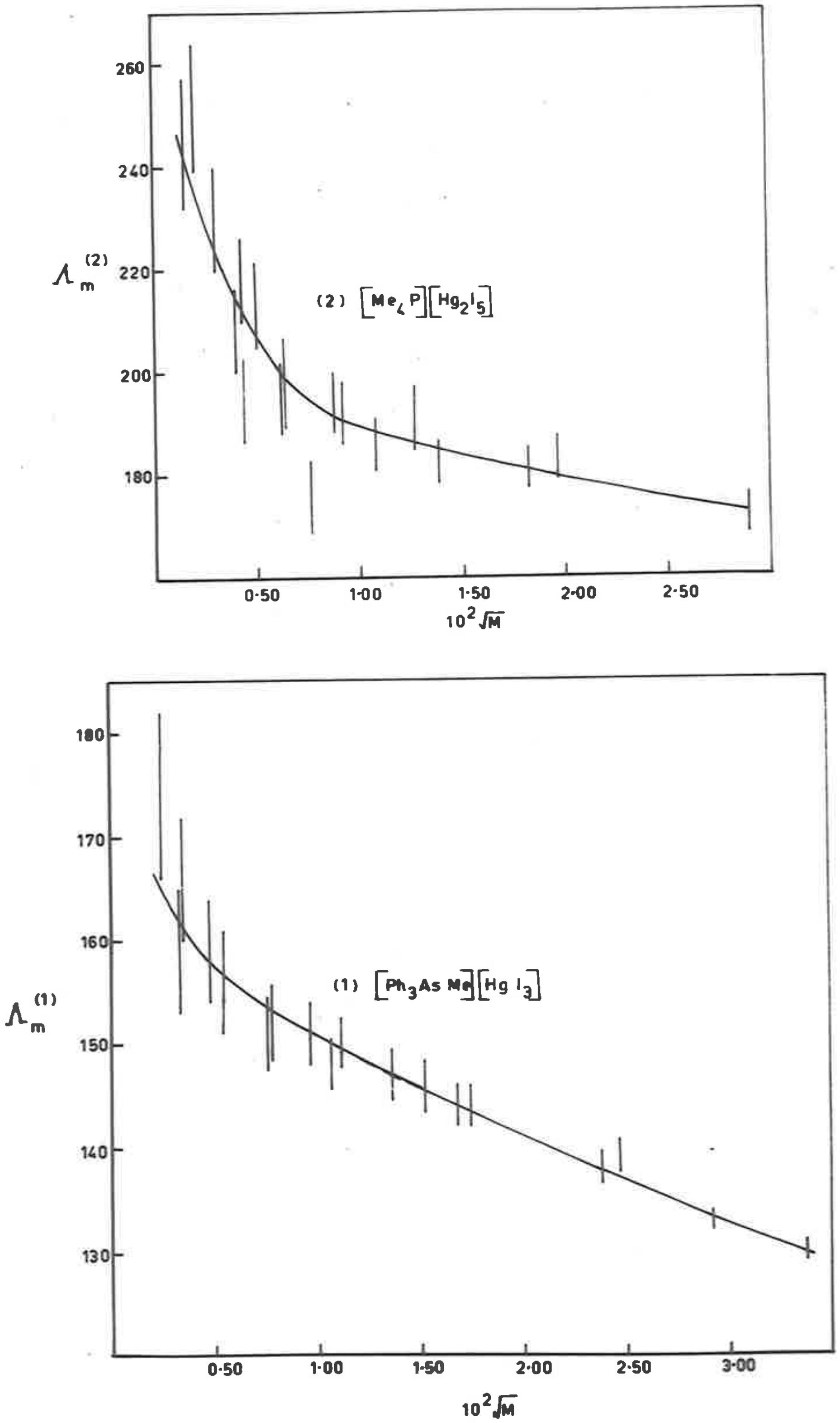


FIG.3.8 CONDUCTIVITIES OF QUATERNARY IODIDES IN ACETONE AT 25°

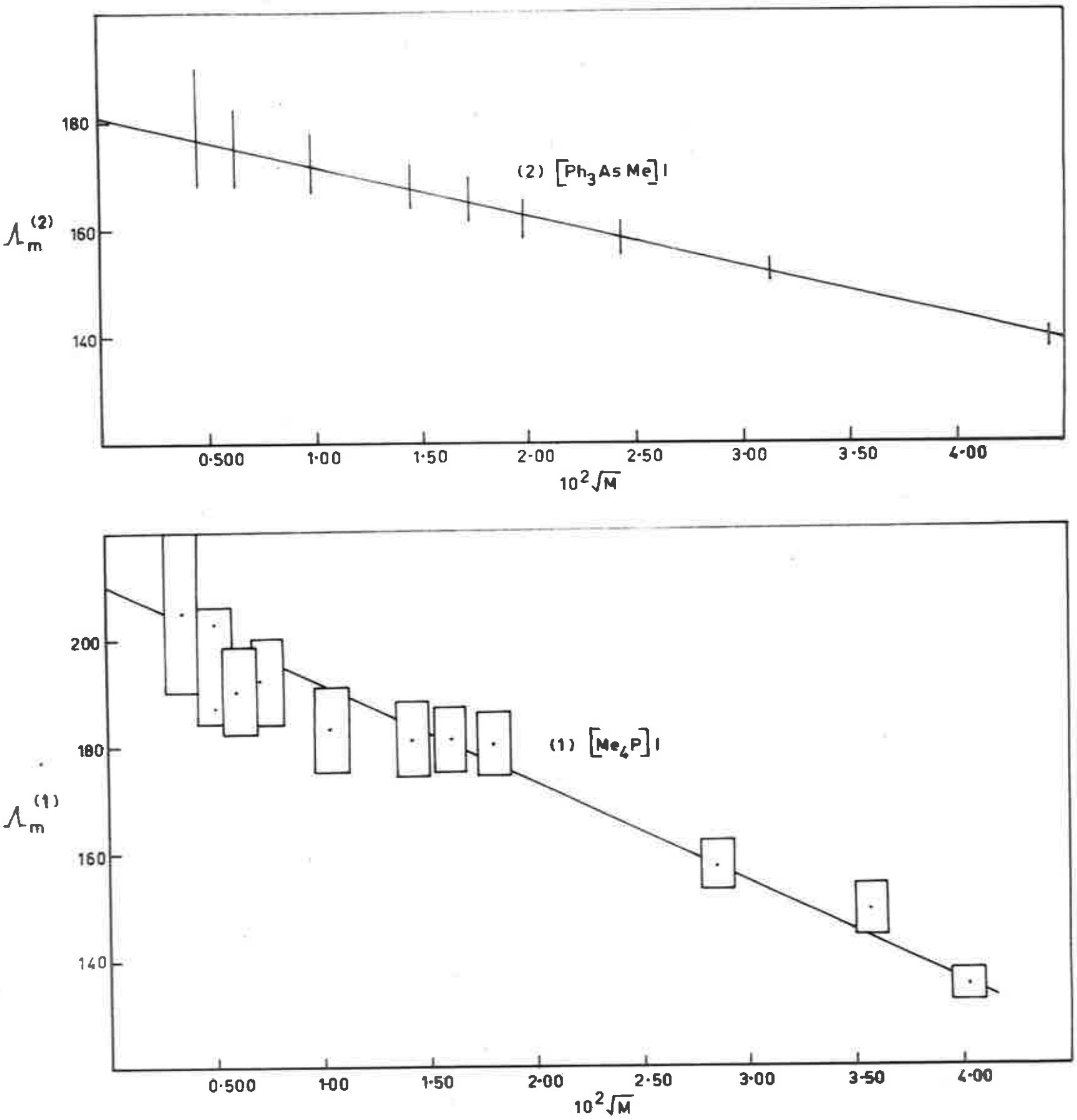
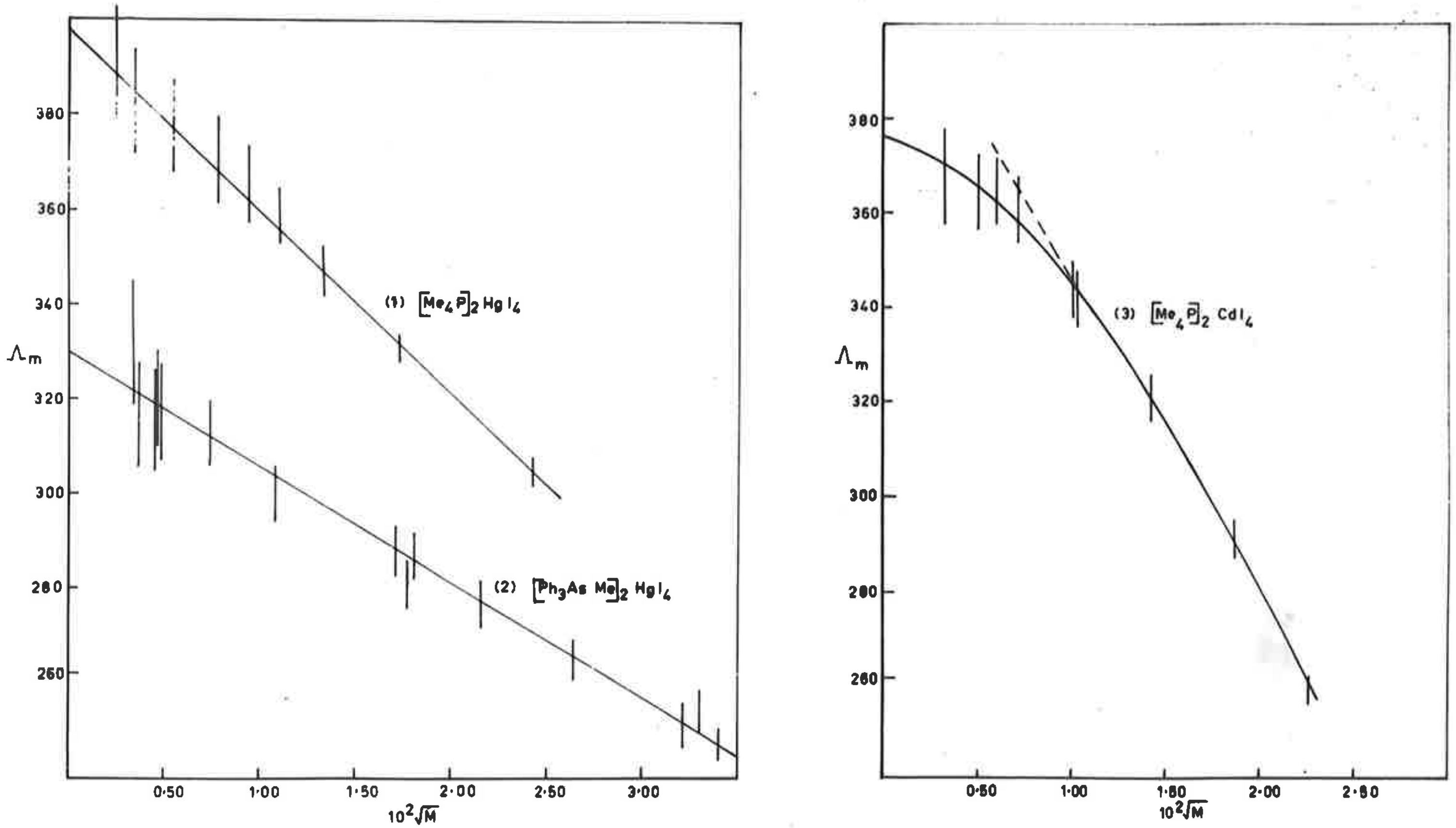


FIG. 3.9 CONDUCTIVITIES OF IODOMERCURATES AND BIS(TETRAMETHYLPHOSPHONIUM) TETRAIODOCADMATE(II) IN ACETONE AT 25°



ate(II) (Fig. 3.6) closely resembles that of the corresponding tetramethylphosphonium compound. Insufficient measurements were obtained at concentrations less than 1 x 10^{-4} M to confirm that this complex shows a sharp rise in conductance at low concentrations. In the concentration region 1-10 x 10^{-4} M the conductances of tetramethylammonium tri-iodomercurate(II) and tetramethylphosphonium tri-iodomercurate(II) are approximately equal at the same concentrations (Table 3.6). This may be understood as the cations are of similar shape and do not differ greatly in size. The approximate ionic diameters as obtained by models are Me_4N^+ 6.3 A, and Me_4P^+ 7.0 A.

TABLE 3.6

Values of the Molar Conductances of $[Me_4N][HgI_3]$ and $[Me_4P][HgI_3]$ for the Concentration Range 1-10 x 10^{-4} M (interpolated from Fig. 3.6).

10^4 M	Molar Conductances	
	$[Me_4N][HgI_3]$	$[Me_4P][HgI_3]$
1.00	181	182
2.25	177	177
4.00	173	173
6.25	169	169
9.00	165	166

Triphenylmethylarsonium tri-iodomercurate(II) has a lower molar conductance than the corresponding tetramethylphosphonium compound at all concentrations investigated (Fig. 3.7), which may be attributed to the greater size of the triphenylmethylarsonium cation.

The molar conductance shows near linear variation with the square root of the molarity in the concentration range 2-11 x 10^{-4} M, and at lower concentrations shows a sharp rise in conductance similar to that of tetramethylphosphonium tri-iodomercurate(II).

The experimental conductances of the tri-iodomercurate complexes cannot be extrapolated to obtain the molar conductances at infinite dilution, due to the curvature of the experimental conductances.

The possibility that the sharp rise in conductance shown by the tri-iodomercurate(II) complexes at low concentrations is due to errors in the solvent correction may be discounted. While the solvent correction is considerable at the lowest concentrations, the upward trend in the conductances is evident at concentrations where the solvent correction is relatively small. In the studies of the conductivity of tetramethylphosphonium tri-iodomercurate(II), the measurements at the lowest concentrations were repeated several times, and the sharp upward trend in the conductances at these concentrations was reproduced with different samples of solvent, varying somewhat in conductivity (details of the purification and conductivities of the acetone are given in Chapter 5).

The molar conductances of triphenylmethylarsonium iodide and tetramethylphosphonium iodide (Fig. 3.8) deviate markedly from the Onsager slopes for these compounds (Table 3.7), hence association to give ion pairs must be considerable. The tetramethylphosphonium compound shows the greater deviation. This cation should form ion pairs more readily than the triphenylmethylarsonium cation due to its smaller size and greater symmetry. The value of the molar conductance at infinite dilution of tetramethylphosphonium iodide, viz., 210 only

TABLE 3.7

Conductivity Properties of Me_4PI and Ph_3MeAsI

Compound	Λ_{m_o}	S	$S_{Onsager}$
Me_4PI	210	1880	700
Ph_3AsMeI	181	940	650

Λ_{m_o}, the molar conductance at infinite dilution, obtained by direct extrapolation of the experimental conductances.

S, the magnitude of the experimental slopes.

$S_{Onsager}$, calculated slopes using the Onsager equation. (Such calculations are a standard procedure, and need not be discussed. The relevant equations for acetone have been reported.[17,18])

differs slightly from that calculated for tetramethylammonium iodide,[19] viz., 218. Such agreement is expected, due to the similarity between the cations, as discussed previously.

A comparison between the Onsager and the experimental slopes cannot be made for the tri-iodomercurate complexes, as the conductances cannot be extrapolated. It is noticeable, however, that the experimental conductances of the three tri-iodomercurate complexes investigated are near parallel in the concentration region $1-10 \times 10^{-4}$ M, despite the difference in the cations. It therefore appears that conductivity effects associated with the dissociation of the tri-iodomercurate ions obscure those due to ion pair formation. In addition the tri-iodomercurate ion is much larger than the iodide ion, for which ion pair formation is markedly dependent on the associated cation, and this increased anion size may reduce the influence of the cation on ion pair formation.

The Complexes Q_2HgI_4 (where Q is a quaternary cation).

The molar conductances of bis(tetramethylphosphonium) tetraiodomercurate(II) and of bis(triphenylmethylarsonium) tetraiodomercurate(II) show linear variation with the square root of the molarity (Fig. 3.9). Direct extrapolation of the experimental conductances gives values of 398 and 330 for the molar conductances at infinite dilution of the respective complexes. There is little evidence for a sharp rise in conductance even at the lowest concentrations studied (cf. the tri-iodomercurate complexes).

The molar conductances are approximately twice the values found for a 1:1 electrolyte at the same concentrations. This is not necessarily evidence for the presence of a 2:1 electrolyte and thus for the presence of the tetraiodomercurate ion, as the magnitude of the conductances may be equally well explained by a mixture of two 1:1 electrolytes. If the tetraiodomercurate ion was the predominant iodomercurate complex at the highest concentrations studied (ca. 10^{-3} M), pronounced curvature of the experimental conductances would be expected at lower concentrations as the extent of dissociation of this compound would increase on dilution. No such curvature was found, and it is concluded that the solutions of the tetraiodomercurate complexes in the concentration range studied contain approximately equimolar amounts of the tri-iodomercurate complex and the quaternary iodide. The failure to observe a sharp rise in conductance at the lowest concentrations similar to that obtained for the tri-iodomercurate complexes may be attributed to a reduction of the dissociation of the tri-iodomercurate ions, due to the presence of the quaternary iodide.

In support of this interpretation of the conductance of tetraiodomercurate complexes, it was shown in the previous section that the tetraiodomercurate ion could not be detected in ethanol and methanol solutions of tetraiodomercurate complexes (ca. 3×10^{-4} M), even in the presence of a moderate excess of added iodide. The equilibrium constant for the reaction, $HgI_3^- + I^- \rightleftharpoons HgI_4^{2-}$, at 25° in acetonitrile[20] is only 40. Thus the degree of dissociation of a tetraiodomercurate complex (1×10^{-3} M) in this solvent would be ca. 96%. With this stability pattern established for solvents differing significantly in their dielectric constants (Table 3.8), it is unlikely that a markedly different pattern would be exhibited in acetone, which has a dielectric constant similar to ethanol (Table 3.8).

TABLE 3.8

Dielectric Constants of Some Organic Solvents.[21]

Solvent	Dielectric Constant
Acetone	20.7
Ethanol	24.3
Methanol	32.6
Acetonitrile	36.7

The molar conductance of a tetraiodomercurate complex at infinite dilution in acetone approximates to that of a 1:1 mixture of the tri-iodomercurate complex and the quaternary iodide, however the extrapolation may be slightly displaced due to the dissociation of the tri-iodomercurate ions, even if this dissociation is insufficient to cause curvature of the experimental conductances. At finite concentrations the specific conductivities of a tetraiodomercurate complex are probably not equal to the sum of the specific conductivities of the tri-iodomercurate complex and the quaternary iodide. Besides the normal mixed electrolyte interactions, the compounds have a common cation which should enhance ion pair formation.

Given and Peover[22] studied the conductance of a 2:1 mixture of tetraethylammonium iodide and mercuric iodide in dimethylformamide. The equivalent conductance, plotted as a function of the concentration of $[NEt_4]_2[HgI_4]$ in equivalents/litre, shows curvature throughout the concentration region 1.6-40 x 10^{-3} equivalents/litre and is of the correct magnitude for a 2:1 electrolyte, which is in agreement with the postulation of the tetraiodomercurate ion as the dominant iodomercurate species, at least at the highest concentrations studied.

The Complexes QHg_2I_5 (where Q is a quaternary cation).

The molar conductance of tetramethylphosphonium pentaiododimercurate(II) shows near linear variation with the square root of the molarity in the concentration region 1-9 x 10^{-4} M, but at lower concentrations the conductance rises markedly. In the concentration range 1-9 x 10^{-4} M the differences between the conductances of tetramethylphosphonium tri-iodomercurate(II) and the corresponding pentaiododimercurate are small (Table 3.9), the conductances of the latter being slightly greater. This would not occur if the $Hg_2I_5^-$ ion was the predominant iodomercurate species in solutions of the pentaiododimercurate complex, as the $Hg_2I_5^-$ ion would have a smaller mobility and thus lower conductance than the HgI_3^- ion due to its greater size. The observed relationship is, however, consistent with dissociation of the

TABLE 3.9

Values of the Molar Conductance of $[Me_4P][HgI_3]$ and $[Me_4P][Hg_2I_5]$ in the Concentration Range $1\text{-}9 \times 10^{-4}$ M, as interpolated from Fig. 3.7, 3.6.

10^4 M	Molar Conductances $[Me_4P][HgI_3]$	 $[Me_4P][Hg_2I_5]$*
1.00	182	189
2.25	177	184
4.00	173	179
6.25	169	175

* These values are less accurate than those of the tri-iodomercurate complex.

pentaiododimercurate complex into the corresponding tri-iodomercurate complex and mercuric iodide at the concentrations studied, $[Me_4P][Hg_2I_5] \longrightarrow Me_4P^+ + HgI_3^- + HgI_2$. The sharp rise in conductance at low concentrations, which is greater than that obtained for the tri-iodomercurate complexes, is due to the formation of approximately a mole of mercuric iodide per mole of pentaiododimercurate complex. A similar stability pattern has been observed for pentaiododimercurate complexes in acetonitrile,[20] ethanol, and methanol (previous section).

Cavell and Sugden[17] measured the conductivities of a number of quaternary sulphonium and ammonium tri-iodomercurates in acetone in the concentration range 4×10^{-4} M - 2×10^{-2} M. The sulphonium iodomercurates were found to show good agreement with the Onsager law, which was considered indicative of near complete dissociation.[17] The ammonium complexes deviated from the Onsager law in a direction opposite to that expected for ion pair formation. However, it may be doubted whether deviations from the Onsager law can be interpreted in terms of ion pair formation for this concentration region. The conductances of many electrolytes in acetone plotted as a function of the square root of the molarity show curvature, as a consequence of which the deviation from the Onsager law at concentrations greater than 4 x 10^{-4} M appears less than at lower concentrations.[19,23] This "lesser deviation" is fortuitous, and it is meaningless to interpret such deviations from the Onsager law in terms of ion pair formation. Thus the comparisons made by Cavell and Sugden may be meaningless due to the concentration region chosen. Indeed the nature of the deviations obtained for the quaternary ammonium tri-iodomercurate(II) complexes supports this view. In addition the values of the conductance at the lower concentrations studied by Cavell and Sugden would be affected by the dissociation of the tri-iodomercurate ions, as discussed previously.

The molar conductance of bis(tetramethylphosphonium) tetraiodocadmate(II) (Fig. 3.9) at concentrations less than 1 x 10^{-4} M appears to show curvature in the opposite direction to that generally observed for electrolytes in acetone. Since this behaviour is unexpected and since the conductances obtained at higher concentrations, which are more accurate, show approximately linear variation with the square root of the molarity, it is possible that the values obtained at the lower concentrations are in error and that these conductances should follow the dashed line in Fig. 3.9.

3. Reactions with Triphenylphosphine.[24]

Gallais[25] prepared the compounds $MHgI_3.H_2O$ (where M is K and NH_4), and proposed that they were not solvates but contained the tetra-coordinate ion $[HgI_3.H_2O]^-$. However the reasons given are inconclusive. The initial aim of the present study was to prepare an unequivocal example of a complex of the type $[HgI_3.Y]^-$ (where Y is a neutral molecule).

The preparation of the complex $[PyH][Ph_3P.HgI_3]$ was attempted by the reaction between equimolar amounts of pyridinium tri-iodomercurate(II) and triphenylphosphine in acetone. However the reaction was found to yield the known complexes di-iodobis(triphenylphosphine)-mercury(II),[26] and bis(pyridinium) tetraiodomercurate(II) (Chapter 2, p. 39),[1] the former complex being precipitated and the latter being isolated from solution.

$$2[PyH][HgI_3] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [PyH]_2[HgI_4] \tag{3.1}$$

Even when the initial iodomercurate:phosphine mole ratio is 2:1, the complex di-iodobis(triphenylphosphine)mercury(II) is precipitated.

Similar reactions have been found for representatives of each of the other main stoichiometric classes of the quaternary iodomercurates, viz.,

$$[PyH]_2[HgI_4] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + 2[PyH]I \tag{3.2}$$

$$[PyH]_2[Hg_3I_8] + Ph_3P \longrightarrow (Ph_3P.HgI_2) + 2[PyH][HgI_3] \tag{3.3}$$

$$[PyH]_2[Hg_3I_8] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + 2[PyH][HgI_3] \tag{3.4}$$

$$[Me_4P][Hg_2I_5] + Ph_3P \longrightarrow (Ph_3P.HgI_2) + [Me_4P][HgI_3] \tag{3.5}$$

$$[Me_4P][Hg_2I_5] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [Me_4P][HgI_3] \tag{3.6}$$

The iodo(triphenylphosphine)mercury(II) complex is precipitated in each reaction. The various types of these complexes have been discussed (Chapter 1, p. 29). Di-iodo(triphenylphosphine)mercury(II), obtained in reactions 3.3 and 3.5, has been independently prepared by direct reaction between mercuric iodide and triphenylphosphine in benzene. This compound is not sufficiently soluble in suitable solvents to permit the determination of the molecular weight, but is probably the dimeric complex di-μ-iododi-iodobis(triphenylphosphine)dimercury(II), by analogy with the known structure of similar complexes (Chapter 1, p. 30).[26]

There is no simple relationship between the initial phosphine: mercury ratio of the reactants, and that of the iodo(triphenylphosphine)-mercury(II) complex precipitated. Thus di-iodobis(triphenylphosphine)-mercury(II) is obtained in reactions in which the initial phosphine: mercury ratio is 2:1 (reaction 3.2), 1:1 (reactions 3.1 and 3.6), 2:3 (reaction 3.4), and 1:2 (reaction between Ph_3P and $[PyH][HgI_3]$ using this ratio), while di-μ-iododi-iodobis(triphenylphosphine)dimercury(II) is obtained in reactions in which the initial phosphine:mercury ratio is 1:2 (reaction 3.5) and 1:3 (reaction 3.3).

The reaction products may be explained by a dissociation mechanism, in which free mercuric iodide, produced by the dissociation of the iodomercurate complexes, reacts with triphenylphosphine. The products formed depend on the initial ratio of triphenylphosphine to free mercuric iodide. Thus 2:1 ratios or greater give $(Ph_3P)_2HgI_2$, and 1:1 ratios or less give $(Ph_3P.HgI_2)_2$. Ratios intermediate should give mixed products.

In the previous section of this chapter it was deduced from conductivity measurements that the stabilities of iodomercurate complexes in acetone are qualitatively similar to those of the corresponding complexes in acetonitrile,[20] ethanol and methanol (this Chapter, section 1).[1] This stability pattern is now to be used to indicate the likely amounts of free mercuric iodide present in solutions of the various iodomercurate complexes, and thus to indicate the phosphine:free mercuric iodide ratio in the various reaction mixtures, and is found to explain the stoichiometries of the reactions.

It was shown in the conductivity studies that tetramethylphosphonium pentaiododimercurate(II) is extensively dissociated into the tri-iodomercurate complex and free mercuric iodide in acetone. The octaiodotrimercurate ion has not been detected in acetonitrile[20] or in ethanol (this Chapter, section 1), and it is likely that this complex undergoes a similar extensive dissociation to the tri-iodomercurate and mercuric iodide in acetone. It is probable therefore that solutions of the pentaiododimercurate and octaiodotrimercurate complexes contain *ca.* 1 mole of free mercuric iodide per mole of the original complex. Thus in the reactions of these complexes with triphenylphosphine the initial phosphine:free mercuric iodide ratio is the same as the initial phosphine:iodomercurate ratio. The reactions may be represented,

$$\left.\begin{array}{l} {[Me_4P][Hg_2I_5]} \longrightarrow Me_4P^+ + HgI_3^- + HgI_2 \\ \\ {[PyH]_2[Hg_3I_8]} \longrightarrow 2PyH^+ + 2HgI_3^- + HgI_2 \end{array}\right\} \begin{array}{l} nPh_3P + HgI_2 \longrightarrow \\ \qquad (Ph_3P)_nHgI_2 \end{array}$$

where n is 1 and 2.

The tri-iodomercurate ion is the most stable of the anionic iodomercurate complexes (Table 1.3), and its degree of dissociation would be small under the conditions used in the present experiments (Chapter 5). Thus the initial phosphine:free mercuric iodide ratio would have been well in excess of 2:1, which is required for the formation of the observed product, di-iodobis(triphenylphosphine)mercury(II), even in the reaction where the initial phosphine:tri-iodomercurate ratio was 1:2.

It was necessary to heat the reaction mixture to induce reaction between the tetraiodomercurate complex and triphenylphosphine, despite the low solubility of the product $(Ph_3P)_2HgI_2$ in the solvents used (ethanol and acetone). It has been shown by the conductivity studies that extensive dissociation of tetraiodomercurate complexes to tri-iodomercurate complexes occurs in acetone. The iodide ions also formed inhibit subsequent dissociation to free mercuric iodide, so that its concentration is too low for precipitation of $(Ph_3P)_2HgI_2$ to occur at room temperatures. However the stability of iodomercurate complexes decreases with heating,^{20} and under such conditions substantial reaction can be achieved between tetraiodomercurate complexes and triphenylphosphine.

The dissociation mechanism successfully explains the stoichiometries of the observed reactions. Probably the only reasonable alternative is a mechanism involving interaction between triphenylphosphine and the tri-iodomercurate ion, which is the predominant anionic species present in solutions of all the iodomercurate complexes used. However such a mechanism could not explain the stoichiometries of the reactions. The course of the reactions is largely dictated by the low solubility of the iodo(triphenylphosphine)mercury(II) complexes in the solvents used, rather than by the relative stabilities of the iodomercurate(II) and triphenylphosphinemercury(II) complexes.

The yields of the iodo(triphenylphosphine)mercury(II) complexes in these reactions are generally significantly lower than those calculated on the basis of equations 3.1-3.6, despite the low solubility of the precipitated complexes in the solvents used. It is possible that the formation of the complex $[HgI_3.Ph_3P]^-$ occurs in competition with the main reaction. It may be possible to test this hypothesis by the examination of the spectra of reaction mixtures at equilibrium. To do this, it will be necessary to obtain first the spectra of the iodobis(triphenylphosphine)mercury(II) complexes. In this connection the reaction between tetraiodomercurate complexes and triphenylphosphine should provide the best opportunity for the formation of the complex $[HgI_3.Ph_3P]^-$, as the concentration of free mercuric iodide is very low, and the tri-iodomercurate ion would be the predominant anionic species present at concentrations suitable for spectroscopic examination.[1]

When the complexes bis(triphenylethylphosphonium) tetraiodomercurate(II), triphenylmethylphosphonium tri-iodomercurate(II), bis(pyridinium) octaiodotrimercurate(II), and tetramethylphosphonium pentaiododimercurate(II) were reacted with excess triphenylphosphine in boiling ethanol, all the mercuric iodide in the compounds was quantitatively precipitated as di-iodobis(triphenylphosphine)mercury(II), according to the equations,

$$[Ph_3PEt]_2[HgI_4] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + 2[Ph_3PEt]I \qquad 3.7$$

$$[Ph_3PMe][HgI_3] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [Ph_3PMe]I \qquad 3.8$$

$$[PyH]_2[Hg_3I_8] + 6Ph_3P \longrightarrow 3(Ph_3P)_2HgI_2 + 2[PyH]I \qquad 3.9$$

$$[Me_4P][Hg_2I_5] + 4Ph_3P \longrightarrow 2(Ph_3P)_2HgI_2 + [Me_4P]I. \qquad 3.10$$

The reactions may thus be used as an analytical method for the determination of the mercuric iodide (or mercury) content of members of the Q_2HgI_4, $QHgI_3$, $Q_2Hg_3I_8$, and QHg_2I_5 (where Q is a quaternary cation) classes of the quaternary iodomercurates. The liberated quaternary iodide was readily recovered from unreacted triphenylphosphine in reactions 3.8-3.10.

Iodomercurate complexes are useful for the isolation of quaternary compounds from complex reaction mixtures, and decomposition with excess triphenylphosphine provides a satisfactory method for the recovery of the quaternary iodide. For example, in the Grignard preparation of trimethylphosphine[27] from methylmagnesium iodide and phosphorus trichloride considerable amounts of tetramethylphosphonium iodide are formed, which can be recovered from the hydrolysed reaction mixture by precipitation as the tetraiodomercurate complex,[28] and subsequent decomposition of this iodomercurate with triphenylphosphine.

By contrast, the decomposition of bis(triphenylmethylphosphonium) tetraiodocadmate(II) by excess triphenylphosphine to give $(Ph_3P)_2CdI_2$ is incomplete. Here the low solubility of the reactant seems to be the major influence.

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CHAPTER 4

Reactions of Metal Complexes with Alkyl Halides*

1. Halo(triphenylphosphine)mercury(II) Complexes.[1]

The reactions of the halo(triphenylphosphine)mercury(II) complexes studied and the results obtained are collected in Table 4.1. Di-iodobis(triphenylphosphine)mercury(II) reacts with methyl iodide or ethyl iodide under reflux to yield the corresponding bis(triphenylalkylphosphonium) tetraiodomercurate(II) complex.

$(Ph_3P)_2HgI_2 + 2RI \longrightarrow [Ph_3PR]_2[HgI_4]$ where R is Me or Et.

Both the reactant complex and the product are almost insoluble in the alkyl iodide. A similar reaction has been obtained with n-propyl iodide, but the product could not be obtained pure. Di-μ-iododi-iodobis(triphenylphosphine)dimercury(II) similarly reacts with methyl iodide or ethyl iodide, the triphenylalkylphosphonium tri-iodomercurate(II) complex formed being soluble in the alkyl iodide.

$(Ph_3P.HgI_2)_2 + 2RI \longrightarrow 2[Ph_3PR][HgI_3]$ where R is Me or Et.

The reactions of 2:1 and 1:1 arsine, mercuric iodide complexes with methyl and ethyl iodide have also recently been studied,[2] and similar results have been obtained.

The complexes, $(Ph_3P)_2HgX_2$ (where X is Cl or Br), also react with methyl iodide under reflux, with the formation of bis(triphenylmethylphosphonium) tetraiodomercurate(II). The reactions involve

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* All reactions were carried out using excess alkyl halide.

TABLE 4.1

Reactions of Halo(triphenylphosphine)mercury(II) Complexes with Alkyl Halides

Complex	Reagent	Conditions	Product
$(Ph_3P)_2HgI_2$	MeI	1	$[Ph_3PMe]_2[HgI_4]$
$(Ph_3P.HgI_2)_2$	MeI	1	$[Ph_3PMe][HgI_3]$
$(Ph_3P)_2HgBr_2$	MeI	1	$[Ph_3PMe]_2[HgI_4]$
$(Ph_3P.HgBr_2)_2$	MeI	1	$[Ph_3PMe][HgI_3]$
$(Ph_3P)_2HgCl_2$	MeI	2	$[Ph_3PMe]_2[HgI_4]$
$(Ph_3P.HgCl_2)_2$	MeI	1	$[Ph_3PMe][HgI_3]$
$(Ph_3P)_2HgI_2$	EtI	1	$[Ph_3PEt]_2[HgI_4]$
$(Ph_3P.HgI_2)_2$	EtI	1	$[Ph_3PEt][HgI_3]$
$(Ph_3P.HgBr_2)_2$	EtI	1	$[Ph_3PEt][HgI_3]$
$(Ph_3P)_2HgI_2$	<u>n</u>-PrI	1	$[Ph_3P.\underline{n}\text{-}Pr]_2HgI_4$ impure
$(Ph_3P)_2HgI_2$	PhI	1	No product identified
$(Ph_3P)_2HgI_2$	EtBr	1,2,3	No reaction
$(Ph_3P.HgI_2)_2$	EtBr	1,2	No reaction
$(Ph_3P)_2HgBr_2$	EtBr	1,2,3	No reaction
$(Ph_3P.HgBr_2)_2$	EtBr	1	No reaction
$(Ph_3P)_2HgI_2$	<u>n</u>-BuBr	1	$(Ph_3P)_2HgBr_2$
$(Ph_3P)_2HgBr_2$	<u>n</u>-BuBr	1	$[Ph_3P.\underline{n}\text{-}Bu]_3[Hg_2Br_7]$

1. Reflux reagents at the boiling point.
2. Reflux reagents in acetone.
3. Reflux reagents in benzene.

halogen exchange,* in addition to the formation of a quaternary compound.

$$(Ph_3P)_2HgX_2 + 4MeI \longrightarrow [Ph_3PMe]_2[HgI_4] + 2MeX$$

The complexes $(Ph_3P.HgX_2)_2$ (where X is Cl or Br) undergo a similar reaction with methyl iodide, with the formation of triphenylmethylphosphonium tri-iodomercurate(II).

$$(Ph_3P.HgX_2)_2 + 6MeI \longrightarrow 2[Ph_3PMe][HgI_3] + 4MeX$$

The complex di-μ-bromodibromobis(triphenylphosphine)dimercury(II) also reacts with ethyl iodide with the formation of triphenylethylphosphonium tri-iodomercurate(II).

The identity of the compounds obtained in these reactions has been confirmed by their independent synthesis from mercuric iodide and the appropriate quaternary iodide, using methods similar to those described in Chapter 2 for the synthesis of tetramethylphosphonium iodomercurates.

The complexes $(Ph_3P)_2HgX_2$ and $(Ph_3P.HgX_2)_2$ (where X is Br or I) do not react with ethyl bromide under reflux. Addition of solvents (benzene and acetone) to ensure partial solution of the complexes does not induce reaction (Table 4.1), hence failure to react is not due to insolubility in ethyl bromide. The complexes $(Ph_3P)_2HgX_2$ (where X is Br or I) react with methyl iodide despite the virtual insolubility of both reactant and product in methyl iodide.

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* Throughout this chapter, this term is only used to describe reactions in which the interchanging halogens are different.

$(Ph_3P)_2HgI_2$ undergoes halogen exchange with n-butyl bromide with the formation of $(Ph_3P)_2HgBr_2$.

$$(Ph_3P)_2HgI_2 + 2\text{n-BuBr} \longrightarrow (Ph_3P)_2HgBr_2 + 2\text{n-BuI}$$

This reaction is much faster than the subsequent reaction of $(Ph_3P)_2HgBr_2$ with n-butyl bromide. The crude product from the latter reaction gave a compound with analytical composition corresponding to the complex $[\text{n-Bu-PPh}_3]_3[Hg_2Br_7]$ (tris(n-butyltriphenylphosphonium) heptabromodimercurate(II)) on recrystallisation. The formation of this complex is surprising, as the reaction of the analogous complex $(Ph_3P)_2HgI_2$ with ethyl iodide yields a tetraiodomercurate. The weight of crude product, however, was in excess of that calculated for the heptabromo compound alone. Evidently another compound was also present, though it could not be isolated. These observations can be explained if it is assumed that lattice energies favour crystallisation of the heptabromodimercurate rather than the expected tetrabromomercurate. Stoichiometric considerations suggest that triphenyl-n-butylphosphonium bromide is also formed. The reaction may thus be formulated,

$$2(Ph_3P)_2HgBr_2 + 4\text{n-BuBr} \longrightarrow [Ph_3P\text{-n-Bu}]_3[Hg_2Br_7] + [Ph_3P\text{-n-Bu}]Br.$$

Halo(triphenylphosphine)mercury(II) complexes react more completely with alkyl iodides than with alkyl bromides. This can be attributed to two factors. (i) The bond energy of C–Br is greater than that of C–I,[3] and (ii) iodomercurate complexes are more stable than bromomercurate complexes[4,5] (Chapter 1, p. 14, 28). Both factors lead to a lower free energy for the reaction with alkyl iodides.

Though the presence of Hg-Hal bonds has been shown to facilitate C-Hal bond rupture,[6] the failure of $(Ph_3P)_2HgI_2$ to react with iodobenzene shows that the effect in this system is insufficient to cause quaternization to occur. Iodobenzene does not react with triphenylphosphine directly.[7]

Mechanism of the Formation of the Quaternary Halomercurate(II) Complex.

There are two possible mechanisms for the reactions in which halogen exchange does not occur.

(a) Dissociation Mechanism. The complex dissociates to give a free triphenylphosphine molecule, which is quaternized by the alkyl halide. The halide ion so formed then complexes to give the halomercurate; e.g., for the reaction of the complex $(Ph_3P)_2HgX_2$ with the alkyl halide RX (where X is a halogen).

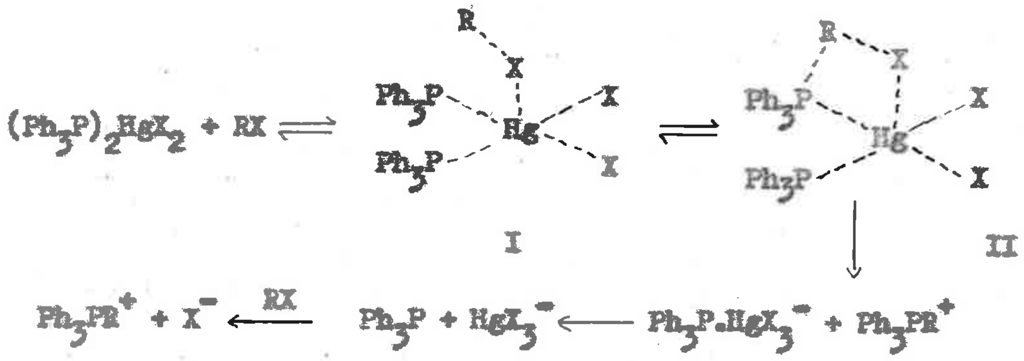
$$\begin{array}{ll}
(Ph_3P)_2HgX_2 \rightleftharpoons Ph_3P.HgX_2 + Ph_3P & \\
Ph_3P + RX \longrightarrow Ph_3PR^+ + X^- & \\
X^- + Ph_3PHgX_2 \rightleftharpoons [Ph_3P.HgX_3]^- & \quad \underline{\text{or}}\ \ Ph_3P.HgX_2 \rightleftharpoons Ph_3P + HgX_2, \\
[Ph_3P.HgX_3]^- \longrightarrow Ph_3P + HgX_3^- & \qquad\qquad\qquad\qquad\qquad\qquad \text{etc.} \\
Ph_3P + RX \longrightarrow Ph_3PR^+ + X^- & \\
X^- + HgX_3^- \rightleftharpoons HgX_4^{\ 2-} &
\end{array}$$

A similar scheme may be written for the reaction of the complex, $(Ph_3P.HgX_2)_2$, with RX.

$$\begin{array}{l}
(Ph_3P.HgX_2)_2 \rightleftharpoons 2Ph_3P.HgX_2 \\
Ph_3P.HgX_2 \rightleftharpoons Ph_3P + HgX_2 \\
Ph_3P + RX \longrightarrow Ph_3PR^+ + X^- \\
HgX_2 + X^- \rightleftharpoons HgX_3^-
\end{array}$$

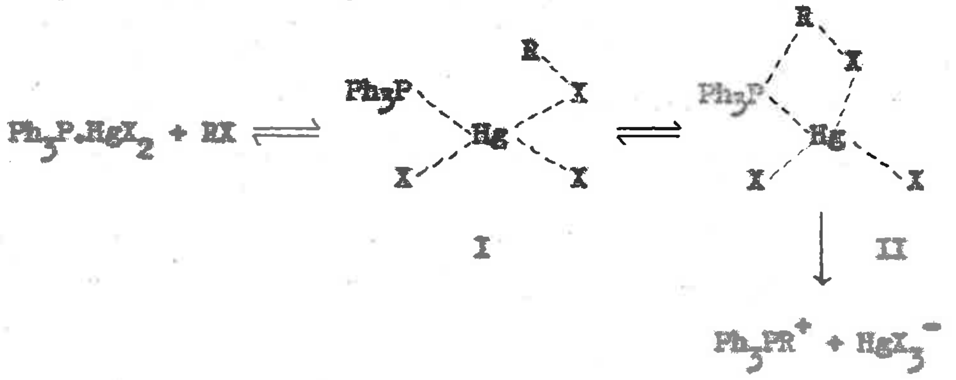
Dissociation of halo(triphenylphosphine)mercury(II) complexes in ethyl bromide must be negligible, as the formation of the cation Ph_3PEt^+ cannot be detected. Triphenylphosphine reacts significantly with ethyl bromide to form triphenylethylphosphonium bromide using comparable conditions, viz., refluxing with excess ethyl bromide (Chapter 5).

(b) *Addition and Rearrangement Mechanism.* An alternate mechanism for these reactions is direct addition of the alkyl halide across the P-Hg bond. Such a mechanism is unlikely in simple form due to the size of the phenyl groups, which probably would prevent the alkyl halide molecule approaching the phosphorus atom sufficiently closely for the direct addition to occur. The reaction may proceed via weak coordination of the alkyl halide to mercury, followed by a rearrangement of the intermediate formed; e.g., for reaction of the complex $(Ph_3P)_2HgX_2$ with the alkyl halide RX (where X is a halogen).

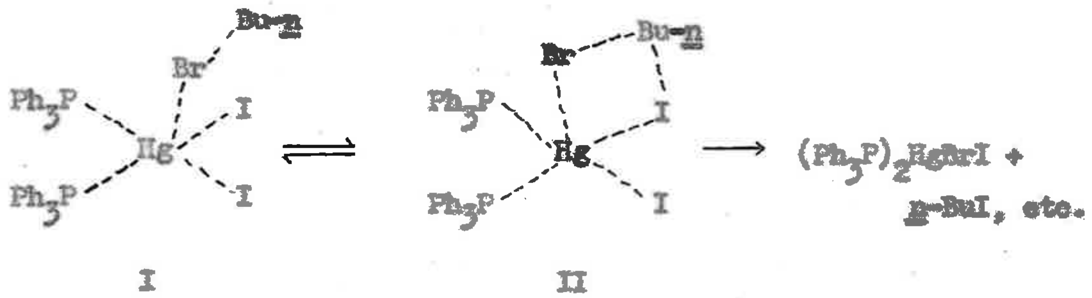


The formation of the intermediate I weakens (and thus lengthens) the P-Hg bond sufficiently to enable the formation of the transition state II by which the addition of the alkyl halide can occur. A similar scheme may be written for $(Ph_3P.HgX_2)_2$ complexes.

$$(Ph_3P.HgX_2)_2 \rightleftharpoons 2Ph_3P.HgX_2$$



The halogen exchange reaction between di-iodobis(triphenylphosphine)mercury(II) and n-butyl bromide may also proceed through an intermediate analogous to I. The weak bonding of the alkyl halide to the mercury also weakens the original Hg-Hal bonds enabling the formation of the halogen exchange transition state, e.g.,



The occurrence of this reaction, in contrast to the behaviour of the complex with ethyl bromide, may be attributed to the higher temperature obtainable on refluxing with n-butyl bromide.

At this stage it is not possible to decide which of mechanisms (a) and (b) operates. It is possible that the two mechanisms contribute to the overall reaction. The use of kinetic measurements in an attempt to decide the mechanism would be difficult, due to the low solubility of the halo(triphenylphosphine)mercury(II) complexes in most solvents. However the use of a different phosphine, e.g., triethylphosphine, or phenyldimethylphosphine, may confer suitable solubility properties.

The Halogen Exchange Reactions.

For the reactions in which halogen exchange occurs in addition to the formation of the quaternary compound, two reaction paths are possible depending on which step occurs first, e.g., for the reaction of the complex $(Ph_3P)_2HgX_2$ with the alkyl halide RY (where X, Y are different halogens).

Path 1 $\quad (Ph_3P)_2HgX_2 \xrightarrow{RY} (Ph_3P)_2HgY_2 \xrightarrow{RY} [Ph_3PR]_2[HgY_4]$

Path 2 $\quad (Ph_3P)_2HgX_2 \xrightarrow{RY} [Ph_3PR]_2[HgX_2Y_2] \xrightarrow{RY} [Ph_3PR]_2[HgY_4]$

An analogous scheme may be written for the reaction of the complex $(Ph_3P.HgX_2)_2$ with the alkyl halide RY.

Path 1 $\quad (Ph_3P.HgX_2)_2 \xrightarrow{RY} (Ph_3P.HgY_2)_2 \xrightarrow{RY} [Ph_3PR][HgY_3]$

or $(Ph_3P.HgY_2)$

Path 2 $\quad (Ph_3P.HgX_2)_2 \xrightarrow{RY} [Ph_3PR][HgX_2Y] \xrightarrow{RY} [Ph_3PR][HgY_3]$

The conversion of di-iodobis(triphenylphosphine)mercury(II) to a bromomercurate must proceed by path 1, as the intermediate formation of dibromobis(triphenylphosphine)mercury(II) has been demonstrated. One possible mechanism for the formation of $(Ph_3P)_2HgBr_2$ has already been considered (see under mechanism (b) above). The possibility that this reaction occurs via dissociation of $(Ph_3P)_2HgI_2$ to mercuric iodide, and halogen exchange between this compound and n-butyl bromide may be discounted. Using conditions similar to those which permit complete halogen exchange between $(Ph_3P)_2HgI_2$ and n-butyl bromide, mercuric iodide is converted by n-butyl bromide to a black solid, which still contains iodine.

The path for the reaction of chloro- and bromo(triphenylphosphine)mercury(II) complexes with alkyl iodides is not certain, as intermediates were not isolated. However, path 2 is definitely possible. The first step is analogous to reactions already shown to occur, while it has been found that bromomercurates and bromoiodomercurates readily undergo halogen exchange with alkyl iodides to yield iodomercurates (see below), hence the second step is possible.

2. Quaternary Halomercurate(II) Complexes.[1]

The observed reactions of these complexes, and a number of related reactions are collected in Table 4.2. Quaternary tribromomercurates, dibromo-iodomercurates, and bromodi-iodomercurates readily undergo halogen exchange with methyl iodide to give the corresponding tri-iodomercurates. The reactions may be summarized by the equation

$$Q[HgBr_nI_{3-n}] + nMeI \longrightarrow Q[HgI_3] + nMeBr$$

where n is 1, 2, and 3, and Q is Ph_3PMe or Ph_3PEt.

In particular it has been shown that triphenylmethylphosphonium dibromo-iodomercurate(II) is converted to the corresponding tri-iodomercurate. This reaction corresponds to the second step of path 2 (see above) for the reaction of $(Ph_3P.HgBr_2)_2$ with methyl iodide. Quaternary tribromomercurates and bromo-iodomercurates also react with ethyl iodide, yielding tri-iodomercurates.

The halogen exchange reactions of tri-iodomercurate complexes with alkyl bromides do not occur readily. Using conditions similar to

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TABLE 4.2

Reactions of Quaternary Halomercurate(II) Complexes and Related Compounds with Alkyl Halides

Complex	Reagent	Conditions	Product
$[Ph_3PEt][HgBr_3]$	MeI	2,3	$[Ph_3PEt][HgI_3]$
$[Ph_3PMe][HgBr_2I]$	MeI	3	$[Ph_3PMe][HgI_3]$
$[Ph_3PMe][HgBrI_2]$	MeI	1	$[Ph_3PMe][HgI_3]$
$[Ph_3PEt][HgBrI_2]$	MeI	3	$[Ph_3PEt][HgI_3]$
$[Ph_3PEt][HgBr_3]$	EtI	1	$[Ph_3PEt][HgI_3]$
$[Ph_3PEt][HgBr_2I]$	EtI	1	$[Ph_3PEt][HgI_3]$
$[Ph_3PEt][HgBrI_2]$	EtI	1	$[Ph_3PEt][HgI_3]$
$[Ph_3PMe][HgI_3]$	EtBr	2	Slight Br substitution
$[Ph_3PMe][HgI_3]$	*n*-BuBr	1	$[Ph_3PMe][HgBrI_2]$
$[Ph_3PEt][HgI_3]$	EtBr	3	No reaction
$HgBr_2$	MeI	1	HgBrI (impure)
$HgBr_2$	MeI	3	Slight I substitution
$[Ph_3PEt]Br$	MeI	3	$[Ph_3PEt]I$
$[Ph_3PEt]Br$	EtI	2	$[Ph_3PEt]I$
$[Ph_3PEt]I$	EtBr	3	$[Ph_3PEt]Br$

1. Reflux reagents at boiling point.
2. Reflux reagents in acetone.
3. Reagents at 25° in acetone.

those which permit complete exchange between triphenylethylphosphonium tribromomercurate(II) and methyl iodide, triphenylethylphosphonium tri-iodomercurate(II) fails to react with ethyl bromide (Table 4.2). Boiling ethyl bromide induces only slight bromination of triphenylmethylphosphonium tri-iodomercurate(II). The more extreme conditions of the reaction using *n*-butyl bromide introduce only one bromine atom/mole of complex.

$$[Ph_3PMe][HgI_3] + n\text{-BuBr} \longrightarrow [Ph_3PMe][HgBrI_2] + n\text{-BuI}$$

The trihalomercurate/alkyl halide exchange reactions can be explained by a dissociation and recombination mechanism of the following type,

$$HgX_3^- \rightleftharpoons HgX_2 + X^- \qquad 4.1$$

$$X^- + RY \longrightarrow RX + Y^- \qquad 4.2$$

$$Y^- + HgX_2 \rightleftharpoons HgX_2Y^- \rightleftharpoons X^- + HgXY \qquad 4.3$$

where $X \neq Y$ and X,Y are Br and I. The dissociations represented by equations 4.1 and 4.3 are well known,[4,8] while the reactions represented by 4.2 have been shown to occur readily under the conditions of the present experiments (Table 4.2; Chapter 5, Section 5.4), and have been the subject of considerable kinetic investigation.[9]

As iodomercurates are more stable than bromomercurates,[4,5,8] it can be explained why tribromomercurates react more completely with alkyl iodides than tri-iodomercurates react with alkyl bromides. The greater stability of the iodomercurate complexes, and the known high stability of the tri-iodomercurate species, favour equilibrium positions to the left hand side of equations 4.1 and 4.3, when X = I and Y = Br;

this inhibits the further dissociation illustrated in equation 4.3, by which complete exchange could occur. In particular the species HgI_2Br^- dissociates into HgI_2 and Br^-, rather than into HgBrI and I^-. By contrast, when X = Br and Y = I, equilibrium positions further to the right of equations 4.1 and 4.3 are favoured; this favours the further dissociation illustrated in equation 4.3. In particular $HgBr_2I^-$ dissociates into HgBrI and Br^-, rather than into $HgBr_2$ and I^-. This explanation accounts for the failure of the HgI_3^-/RBr exchange reactions to proceed beyond the formation of HgI_2Br^-. However, even this first exchange step is far more difficult with tri-iodomercurate complexes than with tribromomercurate complexes. Thus complete exchange occurs between $[Ph_3PEt][HgBr_3]$ and methyl iodide, in 1 hr. at 25°, but no exchange occurs between the corresponding tri-iodomercurate and ethyl bromide. Considering the general equation for the first step in the halogen exchange reactions,

$$HgX_3^- + RY \longrightarrow HgX_2Y^- + RX \qquad 4.4$$

the equilibrium constant for the reaction (K) may be written,

$$K = \frac{[HgX_2Y^-][RX]}{[HgX_3^-][RY]} .$$

Using also the following equilibrium constants,

$$K_f = \frac{[HgX_3^-]}{[HgX_2][X^-]} , \qquad K_g = \frac{[HgX_2Y^-]}{[HgX_2][Y^-]} , \qquad K_h = \frac{[RX][Y^-]}{[RY][X^-]} ,$$

which refer to the reactions, $HgX_2 + X^- \rightleftharpoons HgX_3^-$, $HgX_2 + Y^- \rightleftharpoons HgX_2Y^-$, and $RY + X^- \rightleftharpoons RX + Y^-$, respectively, the equilibrium constant

(K) can be written

$$K = \frac{K_g\,K_h}{K_f}$$

The two specific first step reactions must now be considered, viz.,

$$HgI_3^- + RBr \longrightarrow HgI_2Br^- + RI \qquad 4.5$$

$$HgBr_3^- + RI \longrightarrow HgBr_2I^- + RBr \qquad 4.6$$

The equilibrium constants for the reactions are given by the expressions,

$$K_{4.5} = \frac{K_{g,4.5}\,K_{h,4.5}}{K_{f,4.5}} \;; \qquad K_{4.6} = \frac{K_{g,4.6}\,K_{h,4.6}}{K_{f,4.6}}$$

$K_{f,4.5} > K_{f,4.6}$, as tri-iodomercurates are more stable than tribromomercurates. For the same reason, it is likely that $K_{g,4.6} > K_{g,4.5}$, i.e., the equilibrium constant for the reaction,

$HgBr_2 + I^- \rightleftharpoons HgBr_2I^-$, is greater than that for the reaction

$HgI_2 + Br^- \rightleftharpoons HgI_2Br^-$. Equilibrium lies to the right hand side in the reaction,[10] $Br^- + RI \rightleftharpoons RBr + I^-$, hence $K_{h,4.6} > K_{h,4.5}$. Thus $K_{4.5} < K_{4.6}$, or the equilibrium in reaction 4.5 lies more to the left than in reaction 4.6.

However under the conditions used in the present experiments some detectable exchange between ethyl bromide and triphenylethylphosphonium tri-iodomercurate(II) was expected at 25°. Some dissociation of the tri-iodomercurate ions must occur, and exchange between the iodide ions so formed and the large excess of alkyl bromide used should provide a suitable mechanism for the eventual formation of the $HgBrI_2^-$ complex in high yield, as it has been shown that exchange between iodide ions and a similar large excess of ethyl bromide is complete in 1 hr. at 25°. Thus a kinetic explanation must be sought as to why no exchange between $[Ph_3PEt][HgI_3]$ and ethyl bromide was detectable in 1 hr. at 25°. With the proposed mechanism (equations 4.1–4.3), the overall rate of reactions 4.5 and 4.6 must depend on the rates of the reactions,

$$I^- + RBr \longrightarrow Br^- + RI \qquad 4.7$$

and $$Br^- + RI \longrightarrow I^- + RBr \qquad 4.8$$

respectively. These reactions have been shown to be bimolecular and second order.[10] Thus the rates of reactions 4.7 and 4.8 (and thus 4.5 and 4.6) are given by the expressions,

$$R_{4.5} = R_{4.7} = k_{4.7}\,[I^-][RBr]$$
$$R_{4.6} = R_{4.8} = k_{4.8}\,[Br^-][RI].$$

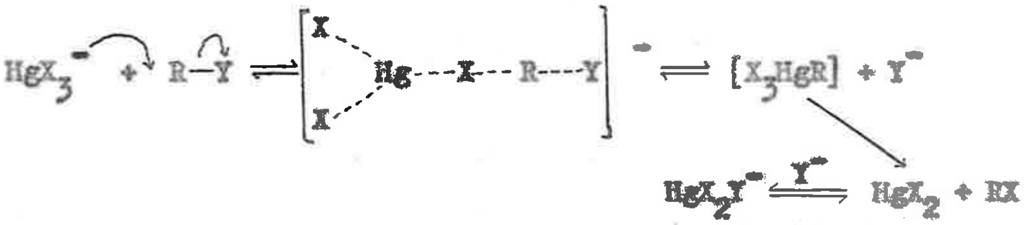
Since a large excess of alkyl halide was used in the reactions its concentration should not alter appreciably during the reactions, hence the expressions reduce to

$$R_{4.5} = k'_{4.7}\,[I^-]$$
$$R_{4.6} = k'_{4.8}\,[Br^-].$$

As the iodomercurate complexes are more stable than the bromomercurate complexes, the initial concentration of bromide is greater than that of iodide. It has also been shown[10] that $k_{4.7} < k_{4.8}$ (for the same alkyl group); thus $k'_{4.7} < k'_{4.8}$. (Both $k_{4.7}$ and $k_{4.8}$ decrease as the length of the alkyl chain increases.) These two factors cause the exchange reactions of tribromomercurate complexes with methyl and ethyl iodide to proceed more readily than the exchange reactions of tri-iodomercurate complexes with ethyl bromide. The higher reaction temperature obtained by using *n*-butyl bromide increases the dissociation of the tri-iodomercurate complex thus causing an increased rate of reaction. (It has been shown that the dissociation of halomercurate complexes increases with increased temperature.[11])

The exchange between mercuric bromide and methyl iodide occurs very slowly, and it is considered that exchange between mercuric halides and alkyl halides does not provide an alternative route for substitution. The quaternary cations used are unaffected by the alkyl halide reagents and are not considered to be involved in the reactions.

An alternative mechanism for these reactions, viz., direct reaction of the trihalomercurate ion with the alkyl halide, can be envisaged. However all features of the observed reactions can be explained by the dissociation and recombination mechanism, the steps in which are *known reactions*. Even if direct trihalomercurate/alkyl halide exchange can occur, the dissociation and recombination mechanism must still operate and contribute to the observed reactions. There are two ways in which trihalomercurate ions could react directly with alkyl halides. *Firstly*, reaction may occur by nucleophilic attack of the trihalomercurate ion on the alkyl halide, thus for reaction 4.4,

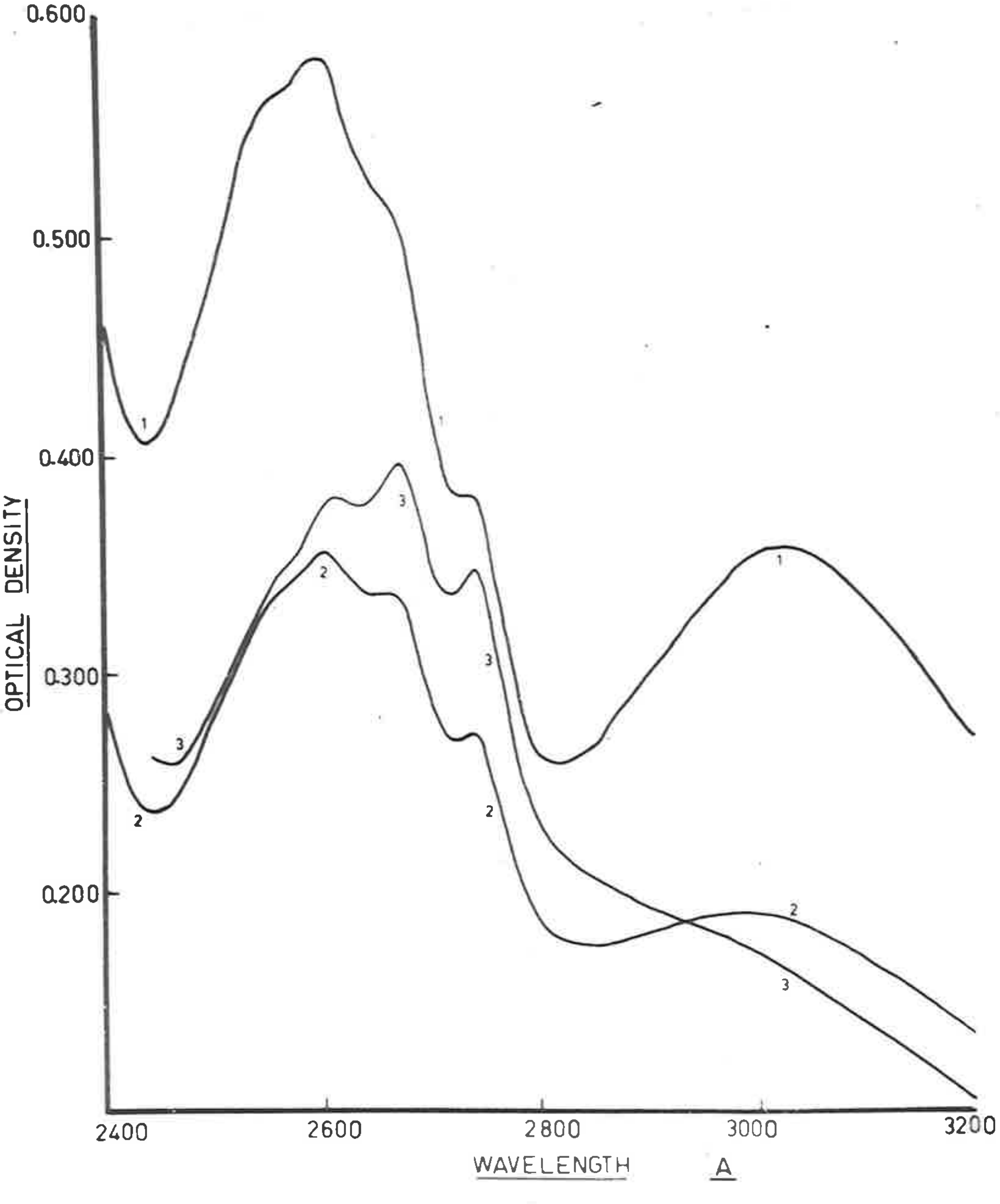


Such a reaction would occur less readily than the corresponding reaction between X^- and RY, as the HgX_3^- ion would be a much weaker nucleophilic reagent than X^-, due to the much greater size of the HgX_3^- ion. The two ions have the same charge, hence the polarizing ability of the HgX_3^- ion would be much lower. In addition this mechanism requires the rupture of a Hg-X bond *in the course of the reaction*, whereas the dissociation and recombination process utilises the halide ions produced by the prior dissociation of the HgX_3^- ions. *Secondly*, the mechanism for reaction 4.4 may involve an intermediate of the type $[\overset{\delta+}{R} \ldots\ldots \overset{\delta-}{HgX_3Y}]^-$ or $R^+HgX_3Y^{2-}$, as the intermediates are analogous to those proposed for the Friedel-Craft reaction. However there is a fundamental difference between the formation of the intermediates in the two cases. The dipole of the alkyl halide $\overset{\delta+}{R} - \overset{\delta-}{Y}$ and the charge on the trihalomercurate ion are such as to oppose the formation of the intermediate, a situation that does not apply in the formation of the Friedel-Craft intermediate.

Ultra-violet Spectra.

In connection with these studies, the ultra-violet spectra of triphenylmethylphosphonium tri-iodomercurate(II), triphenylmethylphosphonium bromodi-iodomercurate(II), and the partially brominated compound from the reaction of the tri-iodomercurate with ethyl bromide, have been measured in methanol (Fig. 4.1). The spectrum of the bromodi-iodomercurate shows no feature that can be conclusively attributed to the formation of the $HgBrI_2^-$ ion, thus the dissociation $HgBrI_2^- \rightleftharpoons HgI_2 + Br^-$ must be considerable. (This dissociation, rather than $HgBrI_2^- \rightleftharpoons HgBrI + I^-$ is proposed because of the relative stabilities of the bromomercurate and iodomercurate complexes.[4,5,8]) The maxima at 2610-2620 A, 2670 A, and 2740 A are close to those given for the triphenylmethylphosphonium cation in ethanol,[12] and must be attributed

Fig. 4.1. Absorption Spectra in Methanol.



1. $[Ph_3PMe]HgI_3$, 3.31×10^{-4}M.
2. Reaction product of $[Ph_3PMe]HgI_3$ and EtBr, ca. 2.6×10^{-4}M.
3. $[Ph_3PMe]HgBrI_2$, 3.66×10^{-4}M.

to this cation. The mercuric iodide maximum at 2700-2710 A [13] cannot be seen. However this is a broad band (Fig. 3.2, curve 1), and is consequently hidden by the sharp changes in absorption exhibited by the cation in the same region. The spectrum of the tri-iodomercurate is similar to that of tetramethylphosphonium tri-iodomercurate(II)[13] (Fig. 3.1, curve 4), both complexes showing a maximum at 3020-3040 A. ($\varepsilon_{[Me_4P][HgI_3]} = 1.09 \times 10^4$, $\varepsilon_{[Ph_3PMe][HgI_3]} = 1.08 \times 10^4$.) The observed differences between the spectra at lower wavelengths may be attributed to the absorption of the triphenylmethylphosphonium cation. The spectrum of the product from the reaction of $[Ph_3MeP][HgI_3]$ with boiling ethyl bromide is intermediate between those of the tri-iodomercurate and the bromodi-iodomercurate. The HgI_3^- band at *ca.* 3000 A is still present, though it is weaker and somewhat displaced towards lower wavelengths.

It is probable that anionic metal halide complexes other than those of mercury will undergo halogen exchange with alkyl halides. Provided such complexes dissociate significantly into free halide ions the exchange is possible. In this connection it has been found that bis(tetraethylammonium) tetrabromocobaltate(II) reacts with ethyl iodide in acetone to give the corresponding tetraiodocobaltate(II) complex. The reaction may be reversed by *n*-butyl bromide.

3. Halo(triphenylphosphine)cadmium(II) Complexes.

The complexes used in this investigation were dibromo- and di-iodobis(triphenylphosphine)cadmium(II). Attempts to prepare the 1:1 complex between cadmium bromide and triphenylphosphine for these studies were unsuccessful. Reaction between triphenylphosphine and cadmium bromide in the correct stoichiometric proportions for the formation of this complex gave $(Ph_3P)_2CdBr_2$.

Di-iodobis(triphenylphosphine)cadmium(II) reacts readily with methyl iodide with the formation of bis(triphenylmethylphosphonium) tetraiodocadmate(II).

$$(Ph_3P)_2CdI_2 + 2MeI \longrightarrow [Ph_3PMe]_2[CdI_4] \tag{4.9}$$

The product has been independently synthesised by reaction between triphenylmethylphosphonium iodide and cadmium iodide. It has, however, not been possible to obtain bis(triphenylmethylphosphonium) tetraiodocadmate(II) completely pure. The formation of the triphenylmethylphosphonium cation in the reaction between $(Ph_3P)_2CdI_2$ and methyl iodide has been confirmed by reaction of the product with mercuric iodide (2 mole of mercuric iodide/mole of product assumed to be $[Ph_3PMe]_2[CdI_4]$), when triphenylmethylphosphonium tri-iodomercurate(II) was obtained in high yield.

$$[Ph_3PMe]_2[CdI_4] + 2HgI_2 \longrightarrow 2[Ph_3PMe][HgI_3] + CdI_2$$

The course of the latter reaction can be understood as iodomercurate complexes are more stable than iodocadmate complexes.[4,8,14] Previous workers have been unable to achieve reaction between di-iodobis(tertiary phosphine)cadmium(II) complexes and methyl iodide.[15]

Dibromobis(triphenylphosphine)cadmium(II) reacts with methyl iodide with the formation of bis(triphenylmethylphosphonium) tetraiodocadmate(II).

$$(Ph_3P)_2CdBr_2 + 4MeI \longrightarrow [Ph_3PMe]_2[CdI_4] + 2MeBr \tag{4.10}$$

The reaction is similar to that exhibited by the corresponding mercury complex, and likewise involves halogen exchange in addition to quaternisation. The identity of the product in this reaction was also confirmed by conversion of the product to the complex $[Ph_3PMe][HgI_3]$.

Reactions 4.9, 4.10 were repeated several times, with and without added solvents, and it was found that the weight of crude product consistently exceeded that calculated for complete reaction. (The complete details are given in Chapter 5, Table 5.2.) It has been shown that this is not caused by subsequent reaction of the product with methyl iodide, e.g., methyl substitution of the phenyl rings of the cation, catalysed by the presence of cadmium-halogen bonds. Bis(triphenylmethylphosphonium) tetraiodocadmate(II), obtained by reaction between triphenylmethylphosphonium iodide and cadmium iodide, does not increase in weight and is recovered unchanged after being refluxed with methyl iodide. The possibility of reaction between triphenylphosphine (produced by dissociation of the halo(triphenylphosphine)cadmium(II) complexes) and acetone (used as a solvent in some reactions) has been eliminated. No instability was noted in the measurement of the spectrum of triphenylphosphine in ethanol,[12] hence it is unlikely that reaction occurs between triphenylphosphine and this solvent. Some free iodine is certainly present in the crude product. It has been shown that tribromomercurates and tetrabromomercurates react with bromine thus,[11]

$$HgBr_3^- + Br_2 \rightleftharpoons HgBr_5^-, \quad HgBr_4^{2-} + Br_2 \rightleftharpoons HgBr_6^{2-},$$

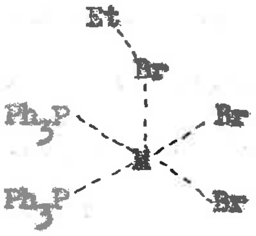
and it is possible that similar reactions may occur between iodine and iodocadmates. However this may not account for all the excess. A further possibility is that iodine formed by decomposition of methyl iodide, or products of reaction between iodine and acetone or ethanol compete with methyl iodide in reacting with the halo(triphenylphosphine)-cadmium(II) complexes. In the former case a triphenyliodophosphonium iodocadmate would be formed initially, which may react further. Analogous mercury complexes are known[16] and are to be discussed (Chapter 6). $(Ph_3P)_2MI_2$ (where M is Hg or Cd) complexes, suspended in acetone, dissolve on the addition of iodine, and further work is intended on these reactions. The use of a different solvent is desirable, however, as some iodine/acetone interaction occurs.

No reaction could be achieved between halo(triphenylphosphine)-mercury(II) complexes and ethyl bromide, however both dibromo and di-iodo-bis(triphenylphosphine)cadmium(II) complexes react with ethyl bromide with the formation of bis(triphenylethylphosphonium) tetrabromocadmate(II).

$$(Ph_3P)_2CdBr_2 + 2EtBr \longrightarrow [Ph_3PEt]_2[CdBr_4]$$
$$(Ph_3P)_2CdI_2 + 4EtBr \longrightarrow [Ph_3PEt]_2[CdBr_4] + 2EtI$$

The Mechanism of the Reactions.

The two mechanisms discussed for the reactions of halo(triphenylphosphine)mercury(II) complexes with alkyl halides are relevant to a discussion of the mechanism of reaction of the cadmium complexes. A choice between the mechanisms for the reactions with alkyl iodides is not possible. However the mechanism of the reactions of ethyl bromide with the cadmium complexes appears clear. The coordination and rearrangement mechanism postulates the intermediate



where M is Cd, Hg,

in reactions of dibromobis(triphenylphosphine)cadmium(II) or mercury(II) complexes. The intermediate is related to the tribromomercurate and tribromocadmate complexes, in that it contains three M-Br bonds. If the stabilities of the intermediates show the same relationship as do those of the tribromo complexes, where $CdBr_3^-$ is less stable than $HgBr_3^-$ ~~complexes~~,[4,8,17] it may be concluded that the formation of the intermediate is more energetically favoured when M = Hg. Since reaction does not occur at all between the bromo(triphenylphosphine)-mercury(II) complexes and ethyl bromide, it is unlikely that this mechanism is used in the reaction of $(Ph_3P)_2CdBr_2$ and ethyl bromide. Thus this reaction probably occurs by the dissociation mechanism,

$$(Ph_3P)_2CdBr_2 \rightleftharpoons (Ph_3P.CdBr_2) + Ph_3P$$
$$Ph_3P + EtBr \longrightarrow [Ph_3PEt]^+Br^-$$
$$Br^- + (Ph_3P.CdBr_2) \rightleftharpoons [Ph_3P.CdBr_3]^- \longrightarrow CdBr_3^- + Ph_3P, \text{ etc.}$$

The yield in the reaction between $(Ph_3P)_2CdBr_2$ and ethyl bromide is similar to that obtained in the direct reaction of triphenylphosphine and ethyl bromide using comparable conditions, which observation is consistent with the dissociation mechanism. The failure of the mercury complexes to react by such a mechanism is consistent with the normal stability pattern in which cadmium complexes are less stable than the corresponding mercury ones.[18] A similar argument may be employed to show that the quaternization step in the reaction of

$(Ph_3P)_2CdI_2$ with ethyl bromide also proceeds by a dissociation mechanism.

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CHAPTER 5

Experimental

This chapter is divided into four sections. Section 5.1 contains a description of the general techniques used, while sections 5.2-5.4 contain the detailed experimental results for Chapters 2-4 respectively.

5.1 General Techniques.

Microanalyses.

Except where otherwise stated in the text all analyses were done by the C.S.I.R.O. Microanalytical Laboratories, Melbourne.

Infra-red Spectra.

Infra-red spectra were measured either by Dr. R.A. Jones of the Department of Organic Chemistry, University of Adelaide, using a Grubb-Parsons Model DB1 spectrophotometer fitted with sodium chloride optics, or by Mr. P. Rogasch of Weapons Research Establishment, Salisbury, using a Hilger-Watts Model H-800 spectrophotometer, fitted with potassium bromide optics. All compounds were examined as Nujol or hexachlorobutadiene mulls.

X-ray Powder Photographs.

Powder photographs were taken by Mr. R. Offler of the Department of Geology, University of Adelaide, with a Philips 57 mm. powder camera, using cobalt radiation with an iron filter.

Magnetic Measurements.

Magnetic moments were measured by the Gouy method.

Ultra-violet Spectra.

Ultra-violet spectra were measured with a Unicam SP500 spectrophotometer, using 1 mm. and 1 cm. silica cells. A constant temperature cell housing (SP570) was employed for determinations at 25°, the circulating water being maintained at 25 ± 0.1°. Other measurements were made at *ca.* 20° (Chapter 3) or *ca.* 25° (Chapter 4).

Solvents used (ethanol and methanol) were reagent grade, refluxed over and distilled from sodium hydroxide.

The spectra of the solutions described in Chapter 3 were measured at several intervals of time during a period of 24 hr. after preparing the solutions, and were found to be unchanged on standing. The spectra were checked with two or more independently prepared solutions of similar concentrations.

Conductivity Measurements.

Conductivities were measured using a Philips GM 4249/01 conductivity bridge. As the maximum possible error using such a bridge is 1.5-3% (depending on the position of the scale used), the measurements were frequently checked with a Wall Model 1 conductivity bridge capable of measuring resistances to 0.1%. (A description of this bridge has been reported by Inman and Jordan.[1]) Agreement between resistances measured using both bridges was better than or equal to 1%.

A conductivity cell of standard design fitted with bright platinum electrodes was used. The cell constant, 0.0132, was determined with 0.001 N aqueous potassium chloride, and the absolute conductivity of the solution was taken from the data of Shedlovsky, Brown, and MacInnes.[2] Conductivity water used in the determination of the cell constant had a conductivity of $1-3 \times 10^{-6}$ ohm^{-1} cm^{-1}.

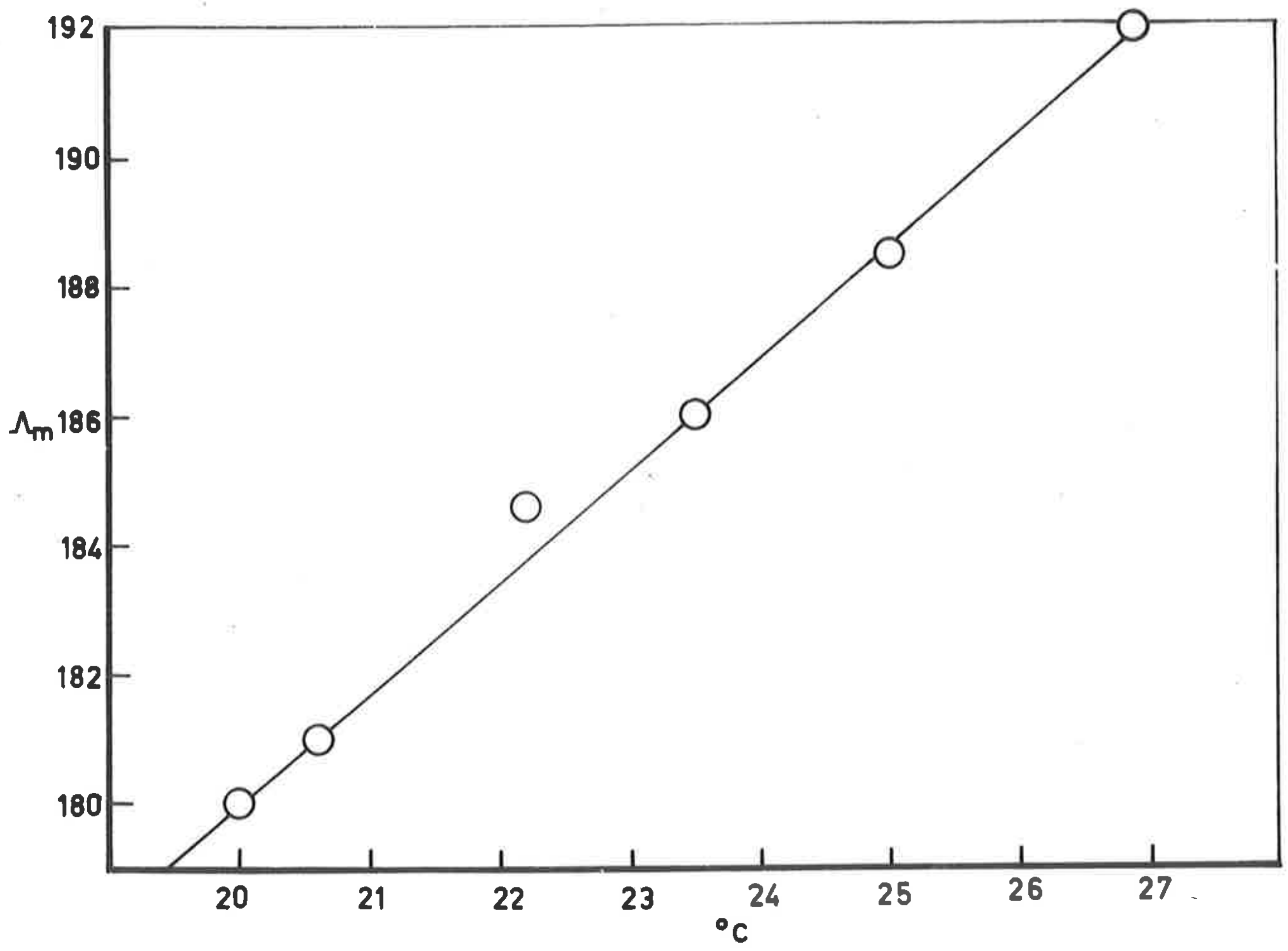
Acetone used in the conductivity measurements was either Analar, dried by potassium carbonate, and distilled, or reagent grade similarly dried and twice distilled, the various samples having conductivities in the range $1-9 \times 10^{-8}$ ohm^{-1} cm^{-1}. Using the Philips bridge, conductivities of solutions were measured at 1000 c/s, while those of solvents were measured at 50 c/s. Using the Wall bridge all measurements were made at 1000 c/s.

For the conductivity measurements the microanalytically pure complexes and quaternary iodides were recrystallized a further time. (Their preparation is given in section 5.2.)

All measurements were carried out at 25 ± 0.05°. In Fig. 5.1 the variation of the conductance of a solution of tetramethylphosphonium tri-iodomercurate(II) with temperature is shown. As the change of conductance with temperature is only ca. two conductance units per degree, any errors introduced by the thermostat variation would be less than 0.2 conductance units.

Solutions for investigation were prepared by dilution of a stock solution. In a given set of measurements, the solvent conductivity was measured first followed by the solutions in order of increasing concentration. This procedure minimises errors due to changes in the solvent conductivity, as the solvent correction for the more concentrated solutions is very small. If a series of conductivity measurements is made with solutions of decreasing concentration, errors may be introduced due to the adsorption of solute on

Fig. 5.1. Variation of the Molar Conductance of Tetramethylphosphonium Tri-iodomercurate(II) (0.228×10^{-4}M) in Acetone with Temperature.



the walls and electrodes of the conductivity cell.

The errors in reproducibility are shown in Fig. 3.6-3.9, and are probably caused by difficulties associated with the ready evaporation of acetone. Some difficulty was experienced in obtaining the conductivities of the most dilute solutions of mercuric iodide (less than 1×10^{-4} M) as the measured resistance was found to increase with time. However it was found that the resistance of a particular solution could be restored to the original value by shaking the solution.

5.2 Properties of the Crystalline Iodomercurate Complexes.

(1) Preparation of Reactants.

The quaternary iodides, tetramethylammonium iodide, tetramethylphosphonium iodide, and triphenylmethylarsonium iodide were required for the preparation of the iodomercurate complexes.

Tetramethylammonium iodide was prepared by the reaction between trimethylamine and methyl iodide in a sealed Carius tube, and, recrystallised from ethanol, had m.p. > 300° (Found: C, 23.9; H, 6.1; I, 63.0. Calc. for $C_4H_{12}IN$: C, 23.9; H, 6.0; I, 63.1%).

Tetramethylphosphonium iodide was prepared by the reaction between trimethylphosphine and methyl iodide in a sealed Carius tube, and, recrystallised from ethanol, had m.p. > 300° (Found: C, 22.2; H, 5.6; I, 58.3. Calc. for $C_4H_{12}IP$: C, 22.0; H, 5.6; I, 58.0%).

Triphenylmethylarsonium iodide was prepared by the reaction between triphenylarsine and methyl iodide, and, recrystallized from ethanol/ether, had m.p. 175-176° (Found: C, 51.0; H, 4.1. Calc. for $C_{19}H_{18}AsI$: C, 50.9; H, 4.1%). After several days the melting point had fallen to 171.5-172°, and was unaltered by further recrystallisation (Found: C, 50.9; H, 4.1; I, 27.9. Calc. for $C_{19}H_{18}AsI$: I, 28.3%). There is some divergence in the literature as to the melting point of this compound, values of 176°,[3,4] 173-174°,[5] 175-176°,[6] and 173°[7] being reported.

(2) Preparation of Quaternary Iodomercurate(II)[8] and Iodocadmate(II) Complexes.

Two general methods were used for the iodomercurate complexes.

Method 1. Stoichiometric amounts of the quaternary iodide and mercuric iodide were heated together in acetone. Though the reactants were sparingly soluble, the products were generally quite soluble. The iodomercurate(II) complexes were isolated either quantitatively by evaporation to dryness, or in high yield by evaporation to crystallisation, frequently after the addition of ethanol to lower the solubility of the complexes.

Method 2. The stoichiometric amount of mercuric iodide dissolved in excess aqueous potassium iodide was added to the stoichiometric amount of the quaternary iodide dissolved in water. The method has been used for the preparation of tetraiodomercurate and tri-iodomercurate complexes. The complex, precipitated in a particular reaction, depends only on the ratio of mercuric iodide to the quaternary iodide, and is independent of the presence of excess potassium iodide provided the reaction mixture is not heated.

All the compounds prepared were recrystallised from acetone, ethanol, or a mixture of the two solvents. The tetraiodomercurate complexes are less soluble in acetone than the other complexes. All the complexes are less soluble in ethanol than in acetone, while the pyridinium complexes are more soluble in acetone and ethanol than the corresponding complexes of the other cations studied.

Bis(tetramethylammonium) tetraiodomercurate(II).- Method 1. Difficulty was experienced in reacting all the quaternary iodide, hence the reactants were boiled together until no more tetramethylammonium iodide would dissolve, when the supernatant liquid was decanted. The crystals of the tetraiodomercurate complex obtained on cooling were filtered off, and the filtrate with added acetone was returned to the unreacted quaternary iodide. This process was repeated until all the tetramethylammonium iodide had reacted. Fine cream needles of the tetraiodomercurate were obtained, m.p. $> 300^\circ$ (lit.,[9] no value given) (Found: C, 11.4; H, 3.0; Hg, 22.8. Calc. for $C_8H_{24}HgI_4N_2$: C, 11.2; H, 2.8; Hg, 23.0%).

Tetramethylammonium tri-iodomercurate(II).- Method 1 gave fine pale yellow needles, m.p. 243° (lit.,[10] 236°) (Found: C, 7.7; H, 1.9; Hg, 30.4. Calc. for $C_4H_{12}HgI_3N$: C, 7.3; H, 1.8; Hg, 30.6%). Method 2 gave a pale yellow powder, m.p. 244° (Found: C, 7.5; H, 1.9; Hg, 30.4%).

Tetramethylammonium pentaiododimercurate(II).- Method 1 gave fine, bright-yellow needles, m.p. 189° (Found: C, 5.0; H, 1.5; Hg, 35.6. $C_4H_{12}Hg_2I_5N$ requires C, 4.3; H, 1.1; Hg, 36.1%).

Tetramethylammonium octaiodotrimercurate(II).- Method 1 gave a bright-yellow microcrystalline powder on complete evaporation of the solvent, m.p. *ca.* 180° (lit.,[9] no value given). On fractional recrystallisation from acetone/ethanol the pentaiododimercurate was first obtained (m.p. and mixed m.p. 189°, after recrystallization from acetone/ethanol) followed by tetramethylammonium tri-iodomercurate(II) (m.p. and mixed m.p. 242.5-244°, after recrystallization).

Bis(pyridinium) tetraiodomercurate(II).- The method of François[11] was used. A cream powder was obtained, m.p. *ca.* 168° (with preliminary softening), (lit.,[11] 159°) (Found: C, 13.9; H, 1.8; Hg, 22.5. Calc. for $C_{10}H_{12}HgI_4N_2$: C, 13.8; H, 1.4; Hg, 23.1%).

Pyridinium tri-iodomercurate(II).- The stoichiometric amounts of bis(pyridinium) tetraiodomercurate(II) and mercuric iodide were reacted in acetone, and the compound crystallized as a yellow microcrystalline powder after the addition of ethanol, m.p. 149.5° (lit.[11,12] 151°, 152-154°) (Found: C, 9.1; H, 1.1; Hg, 29.8. Calc. for $C_5H_6HgI_3N$: C, 9.1; H, 0.9; Hg, 30.3%).

Bis(pyridinium) octaiodotrimercurate(II).- The stoichiometric amounts of the tetraiodomercurate and mercuric iodide required to form the corresponding pentaiododimercurate were heated together in acetone. Mercuric iodide failed to dissolve completely under the conditions used. The resultant solution yielded the octaiodotrimercurate as a yellow microcrystalline powder, m.p. 101.5-102.5° (lit.,[11] 101°) (Found: C, 6.6; H, 0.8; Hg, 34.0. Calc. for $C_{10}H_{12}Hg_3I_8N_2$: C, 6.8; H, 0.7; Hg, 33.9%. Calc. for $C_5H_6Hg_2I_5N$: C, 5.4; H, 0.5; Hg, 36.0%). Reacting the correct proportions of the tri-iodomercurate and mercuric iodide for the formation of the pentaiodo complex in acetone also gave the octaiodo derivative. A deep yellow solid, m.p. *ca.* 130° (reported value[11] of m.p. of [PyH][Hg_2I_5] is 121°), containing more mercuric iodide than required for the formation of the octaiodo complex, could be obtained from ethanol. On addition of acetone, in an attempt to recrystallize, mercuric iodide was deposited.

Bis(tetramethylphosphonium) tetraiodomercurate(II).- Method 1 gave cream needles, m.p. > 300° (Found: C, 11.0; H, 2.9; Hg, 21.9. $C_8H_{24}HgI_4P_2$ requires C, 10.8; H, 2.7; Hg, 22.5%). Method 2 gave a cream powder, m.p. > 300° (Found: C, 10.9; H, 2.8; Hg, 22.3%). Method 2 using ethanol as the solvent for the reactants also gave a cream powder, m.p. > 300°, shown to be the tetraiodomercurate by X-ray powder photographs.

For large scale preparations of this complex it is more satisfactory to utilise the hydrolysed reaction mixture from the Grignard preparation of trimethylphosphine,[13] which has been shown to contain a considerable amount of tetramethylphosphonium iodide.[14] Addition of a solution of mercuric iodide in aqueous potassium iodide to this mixture results in the precipitation of the tetraiodomercurate complex in high yield.

Tetramethylphosphonium tri-iodomercurate(II).- Method 1 gave fine lemon-yellow needles, m.p. 197-197.5° (Found: C, 7.3; H, 2.0; Hg, 29.8. $C_4H_{12}HgI_3P$ requires C, 7.1; H, 1.7; Hg, 29.8%). Method 2 gave a pale yellow powder, m.p. 197-197.5°. The identity of the product was confirmed by mixed m.p. 197.5° and the X-ray powder photograph.

Tetramethylphosphonium pentaiododimercurate(II).- Method 1 gave deep-yellow needles, m.p. 172° (lit.[15,16] 172°) (Found: C, 4.4; H, 1.2; Hg, 35.4. Calc. for $C_4H_{12}Hg_2I_5P$: C, 4.3; H, 1.1; Hg, 35.6%).

Bis(triphenylmethylarsonium) tetraiodomercurate(II).- Method 1 gave cream plates, mp. 167° (Found: C, 34.3; H, 3.0; Hg, 14.5. $C_{38}H_{36}As_2HgI_4$ requires C, 33.8; H, 2.7; Hg, 14.8%).

Triphenylmethylarsonium tri-iodomercurate(II).- Method 1 gave yellow needles, m.p. 139-139.5° (Found: C, 25.3; H, 2.0; Hg, 22.2. $C_{19}H_{18}AsHgI_3$ requires C, 25.3; H, 2.0; Hg, 22.2%).

Triphenylmethylarsonium pentaiododimercurate(II).- The preparation was attempted by method 1 and gave a glue-like product. Extraction with cold acetone gave mercuric iodide and the tri-iodomercurate complex, m.p. and mixed m.p. 140°.

Tetraiodocadmate Complexes.

Bis(pyridinium) tetraiodocadmate(II).- This complex was prepared by the reaction between pyridinium chloride and potassium tetraiodocadmate in water, when it was obtained as a white microcrystalline powder, and, twice recrystallised from ethanol, had m.p. 178-179° (lit.,[9] no value given) (Found: C, 15.4; H, 1.9; I, 63.6 - by macro analysis 63.9. Calc. for $C_{10}H_{12}CdI_4N_2$: C, 15.4; H, 1.5; I, 65.1%).

Bis(tetramethylphosphonium) tetraiodocadmate(II).- This complex was prepared by the reaction between stoichiometric amounts of tetramethylphosphonium iodide and cadmium iodide in acetone, and, recrystallised from acetone/ethanol, had m.p. > 300° (Found: C, 12.3; H, 3.1; Cd, 14.0. $C_8H_{24}CdI_4P_2$ requires C, 12.0; H, 3.0; Cd, 14.0%).

(3) Aqueous Decomposition Reactions.[8]

As both the reactants and the products were essentially insoluble in water, and as the reactions were accompanied by a loss in weight, the observed weight of product in incomplete reactions was in excess of that required for 100% reaction. For such reactions the % yield was calculated assuming that a mixture of the reactant and the product was present.

(a) Tetraiodomercurate Complexes.

A sample of the complex was suspended in water and warmed at ca. 60° (unless stated otherwise) until the cream colour of the suspension had changed to the pale yellow colour of the tri-iodomercurate complex. The aqueous suspension was then cooled, and the product was filtered off, and recrystallized from acetone/ethanol. The identity of the product was confirmed by X-ray powder photographs, the product having a powder photograph identical to that of the same complex prepared by the methods described in Part (2) of this section.

(i) Bis(tetramethylammonium) tetraiodomercurate(II) (0.183 g.) was heated with water (25 ml.) for 10 min., yielding the tri-iodomercurate complex (0.144 g., 98% yield), m.p. and mixed m.p. 244.5°. Iodide was detected in the filtrate after reaction.

(ii) Bis(pyridinium) tetraiodomercurate(II) (0.552 g.) was heated with water (25 ml.) for 15 min., giving the impure tri-iodomercurate complex (0.385 g.), m.p. and mixed m.p. 149-150°. The crude product contained some cream crystals of the unreacted tetraiodomercurate. Evaporation of the filtrate to crystallization gave further tri-iodomercurate (0.064 g.), m.p. 150°, mixed m.p. 149-150°. The total yield was 78%.

When the tetraiodomercurate was heated at 80° in aqueous suspension, a yellow oil slowly formed, which solidified on cooling. After two recrystallizations from acetone/ethanol, the product had m.p.

112° and was not pure. Probably a mixture of the tri-iodomercurate and the octaiodotrimercurate complex was formed.

(iii) Bis(tetramethylphosphonium) tetraiodomercurate(II) (0.171 g.) was heated with water (15 ml.) for 5 min., giving the tri-iodomercurate complex (0.128 g., 99% yield), m.p. and mixed m.p. 197.5°. Iodide was detected in the filtrate.

In a similar experiment a suspension of the tetraiodomercurate complex was boiled with water. After 15 min. the colour of the suspension had changed to bright yellow, the product being the pentaiododimercurate complex, m.p. 173°, mixed m.p. 170°.

(iv) Bis(triphenylmethylarsonium) tetraiodomercurate(II) (0.191 g.) was boiled with water (20 ml.) for 20 min., giving the tri-iodomercurate complex (ca. 0.05 g., 35% yield), m.p. and mixed m.p., 139.5-140°.

(b) Tri-iodomercurate Complexes.

The method used was similar to that for the tetraiodomercurate complexes. The pale-yellow complex was warmed in aqueous suspension until the colour had changed to bright yellow. Again X-ray powder photographs were used to confirm the identity of the products. The products were recrystallised from acetone/ethanol or from ethanol.

(i) Tetramethylammonium tri-iodomercurate(II) (0.240 g.) was heated at ca. 80° with water (30 ml.), yielding the pentaiododimercurate complex (0.193 g., 95% yield), m.p. and mixed m.p. 187.5°.

(ii) Pyridinium tri-iodomercurate(II) (1.324 g.) was heated as a suspension in water (30 ml.) at ca. 80°, until a melt began to form on the bottom of the reaction vessel (15 min.). On cooling the melt solidified, while the amount of crystalline suspension present was increased by crystallization of product from solution. The crystalline precipitate was separated from the solidified melt, and was found to be the octaiodotrimercurate complex (0.553 g.), m.p. 101.5-102.5°, mixed m.p. 102°. The solidified melt (0.341 g.) had m.p. 101.5-103°, mixed m.p. (with the octaiodotrimercurate complex) 100-100.5°, and hence was mainly this compound. When this fraction was treated with acetone, a small amount of mercuric iodide remained after the major proportion of the crystals dissolved. Evidently some further decomposition of the octaiodotrimercurate complex occurred (see below). During the reaction some free pyridine was formed. This may be due to partial decomposition of pyridinium iodide, which is formed in the reaction. The total yield of $[PyH]_2[Hg_3I_8]$ was ca. 75%.

(iii) Tetramethylphosphonium tri-iodomercurate(II) (0.410 g.) was shaken with water (40 ml.) for 1 hr. at room temperature, during which time the colour of the suspension deepened slightly. The suspension was then heated to 80° and was immediately cooled giving the impure pnetaiododimercurate complex (0.365 g., 69% yield). The filtrate was quantitatively analysed for iodide, and it was found that the iodide liberated corresponded to 68% reaction. This established the validity of the methods used to calculate the yields in reactions where the weight of crude product exceeded the theoretical weight of product. In this case the theoretical weight of the product was 0.344 g., cf. 0.365 g. found. The impure product was further degraded by heating with boiling water for 5 min., giving the pentaiododimercurate complex, m.p. and mixed m.p. 172°.

The reaction could be readily completed in one step. The tri-iodomercurate complex (0.122 g.) was degraded by heating with boiling water for 5 min., yielding the pentaiododimercurate complex (0.096 g., 94% yield), m.p. 172-173°, mixed m.p. 171°.

The Effect of Added Iodide.

Tetramethylphosphonium tri-iodomercurate(II) (0.229 g.) was heated with a solution of potassium iodide (2.68 g.) in water (20 ml.). The complex dissolved on heating to 80°, and on cooling bis(tetramethylphosphonium) tetraiodomercurate(II) (0.058 g., 38% yield) crystallised, m.p. > 300°.

(iv) Triphenylmethylarsonium tri-iodomercurate(II) was recovered unchanged, m.p. and mixed m.p. 138.5-139°, after being heated with water for 35 min. at ca. 80-100°, and being vigorously boiled for a further 5 min. This treatment was considerably more severe than that required to decompose the other tri-iodomercurate complexes (i-iii).

In the decomposition of bis(pyridinium) tetraiodomercurate(II) and pyridinium tri-iodomercurate(II) some of the complex product, pyridinium tri-iodomercurate(II) and bis(pyridinium) octaiodotrimercurate(II) in the respective reactions, crystallised from solution on cooling. This may be due to the presence of iodide ions formed in the reactions, rather than to any tendency of the complex products to dissolve in water. Due to experimental difficulties these reactions were carried out using greater amounts of the reactant complexes than in the studies of the complexes of the other cations. This would lead to a higher concentration of liberated iodide. In addition, the decomposition of the tri-iodomercurate complex was accompanied by the formation of pyridine, which should aid the solution of the octaiodo complex formed, as the pyridinium complexes are readily soluble in pyridine.

(c) Other Reactions Attempted.

(i) Tetramethylphosphonium pentaiododimercurate(II) underwent a slow decomposition to mercuric iodide on prolonged boiling with water.

(ii) Bis(pyridinium) octaiodotrimercurate(II) underwent a similar reaction, some pyridine also being formed.

(iii) Bis(pyridinium) tetraiodocadmate(II) was recrystallised unchanged from water, m.p. 178.5-179°, mixed m.p. 179-179.5°.

(d) The decomposition of a single crystal of bis(tetramethylphosphonium) tetraiodomercurate(II) (Chapter 2, p. 51) was studied using a polarising microscope. The single crystal was treated with water at *ca.* 60°.

5.3 Solution Properties of Iodomercurate Complexes.

Reactions of Quaternary Iodomercurate(II) Complexes with Triphenylphosphine.[17]

(a) Reactions with Specific Stoichiometries of Triphenylphosphine.

After reactions (i), (v), (vii), (viii) (below) the products were shown to be identical with authentic samples of the appropriate compounds by comparison of X-ray powder photographs.

In reactions (i-vi) solutions of the required amounts of triphenylphosphine and the quaternary iodomercurate, each in (*ca.* 10 ml.) of acetone, were mixed. Rapid precipitation of an iodo (triphenylphosphine)mercury(II) complex occurred. The mixture was left for an hour, then the precipitate was filtered off (fraction A). The filtrate was evaporated and the residue leached with a small quantity of cold acetone. This dissolved the iodomercurate, leaving undissolved some additional iodo(triphenylphosphine)mercury(II) complex (fraction B). Complete removal of the latter complex from the iodomercurate proved difficult, presumably since triphenylphosphine was reacting further in the extract. A further evaporation and extraction, followed by two or more recrystallizations of the iodomercurate from ethanol [ethanol/ether in the case of pyridinium tri-iodomercurate(II)], were generally necessary to achieve satisfactory purity. The two crops of the iodo(triphenylphosphine)mercury(II) complex were either mixed and recrystallized from boiling benzene or were recrystallized and characterized separately. The stated yields of this complex refer to fraction (A).

Di-iodobis(triphenylphosphine)mercury(II) was synthesized by reaction between stoichiometric quantities of mercuric iodide and triphenylphosphine in benzene (lit.,[18] ethanol used) and, recrystallized from benzene, had m.p. 246-247° (lit.,[18] ca. 250°) (Found: C, 44.0; H, 3.3; I, 26.4. Calc. for $C_{36}H_{30}HgI_2P_2$: C, 44.1; H, 3.1; I, 26.0%).

Di-iodo(triphenylphosphine)mercury(II)* was synthesized by the reaction between stoichiometric amounts of mercuric iodide and triphenylphosphine in benzene and, recrystallized from benzene, had m.p. 242-242.5° (Found: C, 30.6; H, 2.2; I, 35.4. $C_{18}H_{15}HgI_2P$ requires C, 30.2; H, 2.1; I, 35.4%). Di-iodo(triphenylphosphine)mercury(II), m.p. 242° (Found: C, 30.0; H, 2.3; I, 35.3%), was also obtained

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* Probably the dimer, di-μ-iododi-iodobis(triphenylphosphine)dimercury(II) (see Chapter 3, p. 83).

when triphenylphosphine and mercuric iodide reacted in benzene in the stoichiometric ratio required for the formation of the complex, $(Ph_3P)_2(HgI_2)_3$. It was almost insoluble in cold acetone and benzene, insoluble in cold ethanol, and sparingly soluble in boiling benzene and acetone. Decomposition occurred during a Rast molecular-weight determination, and the solubility of the complex in boiling chloroform was not sufficient to afford a meaningful value of the molecular weight.

Reactions.

(i) Pyridinium tri-iodomercurate(II) (1.32 g., 2.0 mmoles) with triphenylphosphine (0.52 g., 2.0 mmoles), yielded di-iodobis-(triphenylphosphine)mercury(II) (0.55 g., 0.56 mmoles, 56%). The mixture of fractions (A) and (B) had m.p. 250° (Found: C, 44.1; H, 3.0; I, 26.0%). The other product was bis(pyridinium) tetraiodomercurate(II), m.p. 168°, mixed m.p. 166.5-167°.

(ii) Pyridinium tri-iodomercurate(II) (0.66 g., 1.0 mmole) with triphenylphosphine (0.13 g., 0.50 mmole) yielded di-iodobis-(triphenylphosphine)mercury(II) (0.10 g., 0.10 mmole, 40%), m.p. and mixed m.p. 245° (Found: C, 44.6; H, 3.2%). The reaction mixture was not further investigated.

(iii) Bis(pyridinium) octaiodotrimercurate(II) (0.44 g., 0.25 mmole) with triphenylphosphine (0.13 g., 0.50 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) {0.20 g., 0.20 mmole, 80% based on the reaction $[PyH]_2[Hg_3I_8] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + 2[PyH][HgI_3]$}, m.p. and mixed m.p. 247-248° (Found: C, 44.4; H, 3.2%). The product obtained as fraction B was not investigated. The other product was pyridinium tri-iodomercurate(II), m.p. and mixed m.p. 149-150° (Found: C, 9.2; H, 1.0; Hg, 29.9. Calc. for $C_5H_6HgI_3N$: C, 9.1;

H, 0.9; Hg, 30.3%).

(iv) Bis(pyridinium) octaiodotrimercurate(II) (0.89 g., 0.50 mmole) with triphenylphosphine (0.13 g., 0.50 mmole) yielded di-iodo(triphenylphosphine)mercury(II) {0.19 g., 0.27 mmole, 54% based on the reaction $[PyH]_2[Hg_3I_8] + Ph_3P \longrightarrow (Ph_3P.HgI_2) + 2[PyH][HgI_3]$}, m.p. and mixed m.p. 242-242.5° (Found: C, 30.2; H, 2.1%). The product obtained as fraction (B) had m.p. and mixed m.p. 240-240.5° (Found: C, 29.9; H, 2.3%). The other product was pyridinium tri-iodomercurate(II), m.p. and mixed m.p. 149-150° (Found: C, 9.6; H, 1.1; Hg, 29.9%).

The reaction was repeated with double the concentration of each reactant to find whether any di-iodobis(triphenylphosphine)mercury(II) was present in the initially precipitated product. Di-iodo(triphenylphosphine)mercury(II) as obtained fraction (A) was twice recrystallized from benzene, then having m.p. and mixed m.p. 241-241.5° (Found: C, 30.2; H, 2.15%). The mother liquors from each recrystallization were combined, and crystallization from this solution gave white crystals (ca. 30 mg.), m.p. 238° (Found: C, 37.1; H, 2.8%), that may be a mixture of the two iodo(triphenylphosphine)mercury(II) complexes.

(v) Tetramethylphosphonium pentaiododimercurate(II) (1.13 g., 1.0 mmole) with triphenylphosphine (0.52 g., 2.0 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) {0.80 g., 0.82 mmole, 82% based on the reaction $[PMe_4][Hg_2I_5] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [PMe_4][HgI_3]$}. The combined products (A) and (B) had m.p. and mixed m.p. 248-249°. The other product was tetramethylphosphonium tri-iodomercurate(II), m.p. and mixed m.p. 196°.

(vi) Tetramethylphosphonium pentaiododimercurate(II) (1.13 g., 1.0 mmole) with triphenylphosphine (0.26 g., 1.0 mmole) yielded di-iodo(triphenylphosphine)mercury(II) {0.36 g., 0.50 mmole, 50% based on the reaction $[PMe_4][Hg_2I_5] + Ph_3P \longrightarrow (Ph_3P.HgI_2) + [PMe_4][HgI_3]$}, m.p. 241-241.5°, mixed m.p. 240-241° (Found: C, 30.1; H, 2.3%). The same product obtained as fraction (B) had m.p. 239-241° (Found: C, 30.1; H, 2.2%). The other product was tetramethylphosphonium tri-iodomercurate(II), m.p. and mixed m.p. 196.5-197° [Found: HgI_2, 66.9 (by decomposition with excess of triphenylphosphine as described below). Calc. for $C_4H_{12}HgI_3P$: HgI_2, 67.6%].

(vii) When acetone solutions of bis(pyridinium) tetraiodomercurate(II) (0.44 g., 0.51 mmole) and triphenylphosphine (0.26 g., 1.0 mmole) were mixed no precipitate was obtained. The solution was evaporated to dryness, white crystals being deposited as the volume decreased. After the residue had been extracted with warm ethanol, di-iodobis(triphenylphosphine)mercury(II) (0.34 g., 0.35 mmole, 70%) remained; recrystallised three times from benzene, it had m.p. and mixed m.p. 248-249°. No crystals were obtained from the ethanol, but it was shown to contain a pyridinium salt by evolution of pyridine on addition of warm aqueous sodium hydroxide.

(viii) Bis(pyridinium) tetraiodomercurate(II) (0.44 g., 0.51 mmole) was partially dissolved in ethanol (10 ml.), and a solution of triphenylphosphine (0.26 g., 1.00 mmole) in ethanol (10 ml.) was added. A slight cloudiness developed in the supernatant liquid. The mixture was heated at ca. 60°, white crystals being deposited, until the yellow colour of the iodomercurate disappeared from the suspension. The precipitated crystals consisted of di-iodobis(triphenylphosphine)-

mercury(II) (0.38 g., 0.39 mmole, 78%); twice recrystallised from benzene, this had m.p. and mixed m.p. 249-249.5°. Evaporation of the ethanol yielded an oil which, on addition of ether, gave crystals of impure pyridinium iodide that recrystallised with difficulty from acetone [m.p. 171-173° (decomp.)] (Found: I, 61.1. Calc. for C_5H_6IN: I, 61.4%). The ether used to crystallize the pyridinium iodide yielded a small amount of unchanged triphenylphosphine on evaporation.

(b) Decomposition of Quaternary Iodomercurates by Excess of Triphenylphosphine.

Triphenylmethylphosphonium tri-iodomercurate(II) was prepared by reaction between stoichiometric amounts of bis(triphenylmethylphosphonium) tetraiodomercurate(II) (section 5.4) and mercuric iodide and, recrystallized from acetone/ethanol, had m.p. 146-146.5° (Found: C, 26.2; H, 2.1; Hg, 22.9. $C_{19}H_{18}HgI_3P$ requires C, 26.5; H, 2.1; Hg, 23.4%).

In reactions (i)-(iv), boiling ethanol solutions of the iodomercurate and triphenylphosphine [in excess of that required to precipitate all the mercuric iodide of the iodomercurate as $(Ph_3P)_2HgI_2$] were mixed, and di-iodobis(triphenylphosphine)mercury(II) was precipitated. The suspension was maintained at the b.p. of the solvent until the yellow colour disappeared. After cooling, the precipitate was filtered off, washed several times with ethanol, dried, and weighed. In (i)-(iii) the filtrate was evaporated to dryness, and ether was added to crystallise the liberated quaternary iodide and dissolve the excess of triphenylphosphine. The quaternary iodide was recrystallized from ethanol/ether or acetone/ether.

(i) Triphenylmethylphosphonium tri-iodomercurate(II) (0.256 g., 0.298 mmole) with triphenylphosphine (0.509 g., 1.93 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) (0.291 g., 0.297 mmole; 100% yield requires 0.292 g.), m.p. (not recrystallized) and mixed m.p. 249-250° (Found: C, 44.6; H, 3.6%). The other product was triphenylmethylphosphonium iodide, m.p. 183-183.5° (lit.,[19,20] 182-183°, 176-181°) (Found: C, 56.5; H, 4.6; I, 30.8. Calc. for $C_{19}H_{18}IP$: C, 56.4; H, 4.5; I, 31.4%).

(ii) Bis(pyridinium) octaiodotrimercurate(II) (0.482 g., 0.271 mmole) with triphenylphosphine (1.03 g., 3.94 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) (0.792 g., 0.809 mmole; 100% reaction requires 0.796 g.), m.p. (not recrystallized) and mixed m.p. 245-246° (Found: C, 44.1; H, 3.0%). The other product was slightly impure pyridinium iodide, m.p. 171-173° (decomp.) (Found: C, 29.5; H, 3.1; I, 60.2. Calc. for C_5H_6IN: C, 29.0; H, 2.9; I, 61.35%).

(iii) Tetramethylphosphonium pentaiododimercurate(II) (0.455 g., 0.404 mmole) with triphenylphosphine (1.04 g., 3.97 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) (0.788 g., 0.805 mmole; 100% reaction requires 0.790 g.), m.p. (unrecrystallized) and mixed m.p. 248-249.5° (Found: C, 44.2; H, 3.1%). The other product was tetramethylphosphonium iodide, m.p. > 300° (Found: C, 22.5; H, 5.4; I, 57.7. Calc. for $C_4H_{12}IP$: C, 22.0; H, 5.5; I, 58.3%).

(iv) Bis(triphenylethylphosphonium) tetraiodomercurate(II) (0.199 g., 0.154 mmole) with excess triphenylphosphine yielded di-iodobis(triphenylphosphine)mercury(II) (0.150 g., 0.153 mmole; 100% reaction requires 0.151 g.). The filtrate was not investigated.

5.4 Reactions of Metal Complexes with Alkyl Halides.

(a) Reactions of Halo(triphenylphosphine)mercury(II) Complexes and Quaternary Halomercurate(II) Complexes.[21]

Preparation of Halo(triphenylphosphine)mercury(II) Complexes.

The preparation of the iodo(triphenylphosphine)mercury(II) complexes has been described in the previous section.

Chloro and Bromo(triphenylphosphine)mercury(II) Complexes.

These were precipitated on mixing ethanol solutions of the stoichiometric amounts of the mercuric halide and triphenylphosphine.

1. Dibromobis(triphenylphosphine)mercury(II).- White powder, m.p. 258-259° (Found: C, 48.2; H, 3.4; Hg, 22.7. $C_{36}H_{30}Br_2HgP_2$ requires C, 48.8; H, 3.4; Hg, 22.7%).

2. Di-μ-bromodibromobis(triphenylphosphine)dimercury(II).- White powder, m.p. 251-252° (lit.[18] 240-250°) (Found: C, 34.8; H, 2.8. Calc. for $C_{36}H_{30}Br_4Hg_2P_2$: C, 34.7; H, 2.4%).

3. Dichlorobis(triphenylphosphine)mercury(II).- Recrystallised from acetone, white needles, m.p. *ca.* 270° (lit.[18] 273°) (Found: C, 53.8; H, 3.8. Calc. for $C_{36}H_{30}Cl_2HgP_2$: C, 54.3; H, 3.8%).

4. Di-μ-chlorodichlorobis(triphenylphosphine)dimercury(II).- White powder, m.p. *ca.* 300-310° (lit.[18] 306-309°) (Found: C, 40.7; H, 3.05. Calc. for $C_{36}H_{30}Cl_4Hg_2P_2$: C, 40.5; H, 2.8%).

Preparation of Quaternary Halides.

The compounds triphenylmethylphosphonium iodide, and triphenylethylphosphonium bromide and iodide were required for the synthesis of the quaternary halomercurates.

Triphenylmethylphosphonium iodide was prepared by reaction between triphenylphosphine and methyl iodide, and, recrystallised from ethanol/acetone, had m.p. 185° (Found: C, 56.8; H, 4.6%).

Triphenylethylphosphonium iodide was prepared by reaction between triphenylphosphine and ethyl iodide, and, recrystallized from acetone, had m.p. 167-167.5° (lit.,[19] 164-165°) (Found: C, 57.6; H, 4.7; I, 31.0. Calc. for $C_{20}H_{20}IP$: C, 57.6; H, 4.8; I, 30.4%).

Triphenylethylphosphonium bromide was obtained by refluxing triphenylphosphine with excess ethyl bromide. In a typical preparation triphenylphosphine (1.19 g.) was converted to triphenylethylphosphonium bromide (0.87 g., 52%), recrystallized from ether/ethanol, m.p. 204-204.5° (lit.[22] 203.5°) (Found: C, 64.6; H, 5.5. Calc. for $C_{20}H_{20}PBr$: C, 64.7; H, 5.5%), after reacting with ethyl bromide for 10 hr.

Preparation of Quaternary Halomercurates.

All preparations were affected by reaction between stoichiometric amounts of appropriate reagents (the specific reagents used are given in parenthesis after the name of the compound) in acetone. The required complex was crystallized, generally after the addition of ethanol to lower the solubility, and recrystallized from acetone or acetone/ethanol.

1. Triphenylethylphosphonium tribromomercurate(II).- (Ph_3PEtBr-$HgBr_2$). White microcrystalline powder, m.p. 136.5° (Found: C, 32.7; H, 2.8; Hg, 26.9. $C_{20}H_{20}Br_3HgP$ requires C, 32.8; H, 2.7; Hg, 27.4%).

2. Triphenylmethylphosphonium dibromoiodomercurate(II).- (Ph_3PMeI-$HgBr_2$). Cream plates, m.p. 137.5° (Found: C, 29.8; H, 2.4. $C_{19}H_{18}Br_2HgIP$ requires C, 29.8; H, 2.4%).

3. Triphenylethylphosphonium dibromo-iodomercurate(II).-

($Ph_3PEtBr{-}HgI_2{-}HgBr_2$). Fine cream needles, m.p. 119-119.5° (Found: C, 30.9; H, 2.6. $C_{20}H_{20}Br_2HgIP$ requires C, 30.8; H, 2.6%).

4. Triphenylmethylphosphonium bromodi-iodomercurate(II).- ($Ph_3PMeI{-}HgBr_2{-}HgI_2$). Pale yellow fine needles, m.p. 140° (Found: C, 27.9; H, 2.2. $C_{19}H_{18}BrHgI_2P$ requires C, 28.1; H, 2.2%).

5. Triphenylethylphosphonium bromodi-iodomercurate(II).- ($Ph_3PEtBr{-}HgI_2$). Pale yellow microcrystalline powder, m.p. 93-94° (Found: C, 29.0; H, 2.5. $C_{20}H_{20}BrHgI_2P$ requires C, 29.1; H, 2.4%).

6. Triphenylmethylphosphonium tri-iodomercurate(II).- This Chapter, Section 5.3, p. 131.

7. Triphenylethylphosphonium tri-iodomercurate(II).- ($Ph_3PEtI{-}HgI_2$). Yellow needles, m.p. 127.5-128° (Found: C, 27.3; H, 2.3; Hg, 22.7; I, 43.7. $C_{20}H_{20}HgI_3P$ requires C, 27.5; H, 2.3; Hg, 23.0; I, 43.7%).

8. Bis(triphenylmethylphosphonium) tetraiodomercurate(II).- ($Ph_3PMeI{-}HgI_2$). Pale yellow plates, m.p. 172-173° (Found: C, 37.1; H, 2.8. Calc. for $C_{38}H_{36}HgI_4P_2$ requires C, 36.1; H, 2.85%). Further recrystallisation failed to improve the purity of the complex.

9. Bis(triphenylethylphosphonium) tetraiodomercurate(II).- ($Ph_3PEtHgI_3{-}Ph_3PEtI$). Very small, pale yellow plates, m.p. 135-136° (Found: C, 36.9; H, 3.3. $C_{40}H_{40}HgI_4P_2$ requires C, 37.2; H, 3.1%).

(1) Reactions of Halo(triphenylphosphine)mercury(II) Complexes with Alkyl Halides.

The reactions were carried out by refluxing the solid complex (0.2-1 g.) with a large excess of redistilled reagent grade alkyl halide (10-30 ml.). In some reactions an additional solvent was employed.

If the reaction product was insoluble it was filtered off and recrystallised from acetone/ethanol (except in the case of attempted reactions with ethyl bromide). If the product was soluble the solution was evaporated to dryness under reduced pressure and the residue recrystallised from acetone/ethanol.

With Methyl Iodide.

In all reactions the yield was > 90%.

1. $(Ph_3P)_2HgI_2$ was refluxed as a suspension in methyl iodide for 2 hrs. The resulting pale yellow solid precipitated was bis-(triphenylmethylphosphonium) tetraiodomercurate(II), m.p. and mixed m.p. 172-172.5° (Found: C, 36.6; H, 3.1%). The product was converted to the tri-iodomercurate, m.p. and mixed m.p. 146-146.5° (Found: C, 26.4; H, 2.2%) by reaction with mercuric iodide in acetone. The methyl iodide was evaporated and contained negligible solute.

2. $(Ph_3PHgI_2)_2$ dissolved on refluxing to give a yellow solution. After 2 hr. the solvent was evaporated, and triphenylmethylphosphonium tri-iodomercurate(II) was obtained, m.p. and mixed m.p. 146-146.5° (Found: C, 26.8; H, 2.2%).

3. $(Ph_3P)_2HgBr_2$ was refluxed as a suspension for $1\frac{1}{2}$ hr. The yellow precipitate was bis(triphenylmethylphosphonium) tetraiodomercurate(II), m.p. 172°, mixed m.p. 171.5-172° (Found: C, 37.0; H, 3.2%). Conversion to the tri-iodomercurate gave m.p. 145.5-146°, mixed m.p. 146° (Found: C, 26.3; H, 2.2%).

4. $(Ph_3PHgBr_2)_2$ dissolved on refluxing to give a yellow solution. After 1 hr. the solvent was evaporated and triphenylmethylphosphonium tri-iodomercurate(II) was obtained, m.p. 146°, mixed m.p.

146-146.5° (Found: C, 26.7; H, 2.4%).

5. $(Ph_3P)_2HgCl_2$ was refluxed with methyl iodide and acetone. After 5 min. the bulk of the complex had dissolved to give a pale yellow solution, then slow precipitation of pale yellow crystals commenced. After 1 hr. the volatiles were evaporated and bis(triphenylmethylphosphonium) tetraiodomercurate(II) was obtained, m.p. and mixed m.p. 173-173.5° (acetone only) (Found: C, 36.9; H, 3.3%). Conversion to the tri-iodomercurate gave m.p. 146.5-147°, mixed m.p. 146.5° (Found: C, 26.45; H, 2.2%).

6. $(Ph_3P.HgCl_2)_2$ dissolved on refluxing to give a yellow solution. After 2 hr. triphenylmethylphosphonium tri-iodomercurate(II) was obtained, m.p. 146-146.5°, mixed m.p. 146° (Found: C, 26.5; H, 2.4%).

With Ethyl Iodide.

Except in 1, yields of crude product were > 95%.

1. $(Ph_3P)_2HgI_2$ (0.96 g., 0.98 mmole) was refluxed as a suspension in ethyl iodide (25 ml.) for 8 hr. The pale yellow precipitate was bis(triphenylethylphosphonium) tetraiodomercurate(II) (1.03 g., 0.80 mmole, ca. 80%), m.p. 126-130° (by direct synthesis, 135-136°), unaltered by further recrystallization (Found: C, 37.9; H, 3.6%). Evaporation of the ethyl iodide yielded a small amount of pale yellow solid, not further investigated.

2. $(Ph_3P.HgI_2)_2$ dissolved on refluxing to give a yellow solution. After 2½ hr. the ethyl iodide was evaporated and triphenylethylphosphonium tri-iodomercurate(II) was obtained, recrystallized three times from acetone/ethanol, m.p. 131-133° (by alternate synthesis 127.5-

128°) (Found: C, 26.9; H, 2.2; HgI_2, 52.7 (by decomposition of the complex with excess triphenylphosphine). Calc. for $C_{20}H_{20}HgI_3P$: HgI_2, 52.1%).

3. $(Ph_3P.HgBr_2)_2$ dissolved on refluxing to give a yellow solution. The residue, after removal of the solvent, was impure triphenylethylphosphonium tri-iodomercurate(II), m.p. 124-124.5°. 0.402 g. of impure product was decomposed by excess triphenylphosphine in ethanol to yield di-iodobis(triphenylphosphine)mercury(II) (0.436 g., 0.446 mmole, 97% based on $C_{20}H_{20}HgI_3P$), m.p. and mixed m.p. 248-249° (Found: C, 44.1; H, 3.2%) as a precipitate. The ethanol solution was evaporated to dryness, yielding triphenylethylphosphonium iodide (0.178 g., 0.426 mmole, 92%), recrystallised from acetone/ether, m.p. 166°, mixed m.p. 166° (Found: C, 57.7; H, 5.0%), which was separated from unreacted triphenylphosphine. Refluxing the impure triphenylethylphosphonium tri-iodomercurate(II) from the original reaction with more ethyl iodide gave a purer product, m.p. 126-127° (Found: C, 27.2; H, 2.3; I, 44.0%).

With n-Propyl Iodide.

$(Ph_3P)_2HgI_2$ was refluxed with excess n-propyl iodide until a molten pale yellow product began to form. The reaction mixture was allowed to stand for 24 hr. The product was impure bis(triphenyl-n-propylphosphonium) tetraiodomercurate(II), m.p. 90-160° (Found: C, 38.5; H, 3.6; Hg, 14.6; I, 37.8. $C_{42}H_{44}HgI_4P_2$ requires C, 38.2; H, 3.3; Hg, 15.2; I, 38.5%).

With Ethyl Bromide.

The complexes $(Ph_3P)_2HgX_2$ and $(Ph_3P.HgX_2)_2$ (where X is I, Br) were refluxed as suspensions in ethyl bromide. Certain reactions were also attempted in the presence of benzene or acetone to ensure partial solution of the complexes. In most of the experiments the bulk of the reactant was recovered unchanged from suspension by filtration, the results being given in Table 5.1 (nos. 1-7). The filtrate from 2, 3, 4, 6 was evaporated to dryness, the residue obtained being primarily unchanged reactant in each case. No more than a trace of product could be detected. In expt. 8 the volatiles were removed "in vacuo" and the residue extracted with 3 ml. cold acetone. The bulk of the material was insoluble, and was unchanged reactant. The soluble material was also primarily unchanged reactant.

$(Ph_3P)_2HgBr_2$ was also recovered substantially unchanged after refluxing with ethyl bromide in benzene for 2 hr., m.p. 260-261° (Found: C, 48.7; H, 3.5%).

With n-Butyl Bromide.

1. $(Ph_3P)_2HgI_2$ (0.53 g.) was refluxed with *n*-butyl bromide. After 2½ hr. a pale yellow-brown melt formed. This solidified on cooling, and white crystals were deposited from solution. After a further 1½ hr. heating, the product was a white crystalline suspension, which was filtered off (0.53 g.), m.p. 189-190°. On fractional recrystallisation from acetone/ethanol, di-bromobis(triphenylphosphine)mercury(II), m.p. 258-259° and mixed m.p. 258° (after two recrystallizations from acetone) (Found: C, 47.9; H, 3.9%) crystallized first, followed by a much smaller amount of white microcrystalline solid, m.p. 117.5-118° (after two recrystallizations from acetone/ethanol) (Found: C, 36.5; H, 3.2%), not identified. When $(Ph_3P)_2HgI_2$ (0.57 g.) was refluxed with *n*-butyl bromide for 2 hr., the solid product (0.54 g.) was iodine

TABLE 5.1

Attempted Reaction of Complexes with Ethyl Bromide

Expt.	Complex	W_1(g)	Time (hr.) [conditions]	W_2(g)	m.p.° *	Product mixed m.p.	Found %C	Found %H
1	$(Ph_3P)_2HgI_2$	0.73	6[a]	0.67	249-250	250	-	-
2	"	0.56	7[b]	0.47	247-248	247-248	43.8	3.2
3	"	0.40	5[c]	0.36	247-247.5	248-248.5	44.2	3.2
4	$(Ph_3P.HgI_2)_2$	0.14	11[a]	0.10	241-242	241-242	-	-
5	$(Ph_3P)_2HgBr_2$	0.44	14[a]	0.38	258	257-257.5	-	-
6	"	0.37	3.5[c]	0.33	260-260.5	258.5-260	48.8	3.6
7	$(Ph_3P.HgBr_2)_2$	0.64	13[a]	0.62	252-253	252-253.5	-	-
8	$(Ph_3P.HgI_2)_2$	0.47	6[c]	0.41	240.5-241	240-240.5	30.4	2.2

W_1 initial weight complex.
W_2 weight complex recovered (see text).
a reflux with ethyl bromide.
b " " " " in benzene.
c " " " " in acetone.
* Nos, 4,8 recrystallized from benzene, others as isolated.

free and only gave one fraction on recrystallization, viz., impure $(Ph_3P)_2HgBr_2$, m.p. 253°.

2. When $(Ph_3P)_2HgBr_2$ (0.59 g.) was refluxed with n-butyl bromide for 7½ hr., a pale yellow-brown melt slowly formed. On cooling this became semi-solid, and was filtered off. After drying (80°) to remove solvent the product (0.71 g.) did not solidify. Considerable difficulty was experienced in crystallising the product. White crystals were eventually obtained from acetone/ethanol. The product again softened on oven drying to remove solvent, but solidified on cooling. It analysed as tris(triphenyl-n-butylphosphonium) heptabromodimercurate(II), m.p. 111-112° (Found: C, 41.2; H, 3.8; P, 4.8; Hg, 20.5; Br, 29.4. Calc. for $C_{66}H_{72}P_3Hg_2Br_7$: C, 41.3; H, 3.75; P, 4.85; Hg, 20.9; Br, 29.2%). The weight of semi-solid product was in excess of that required for the formation of the heptabromodimercurate alone (0.64 g.). Another compound must also be present.

Attempted Reaction with Iodobenzene.

$(PPh_3)_2HgI_2$ (0.69 g.) was refluxed with iodobenzene for ca. 2 hr. The compound dissolved but no yellow iodomercurate colour developed in the solution. When the iodobenzene was removed by distillation, a pale glue was obtained which could not be crystallized.

(2) Reactions of Quaternary Trihalomercurate(II) Complexes with Alkyl Halides.

For reactions in absence of an added solvent, a considerable excess of alkyl halide (10-20 ml.:0.1-0.6 g. complex) was employed. Where acetone was added 0.1-0.4 g. complex was initially dissolved in 10 ml. of acetone and 5 ml. (nos. 1, 2, 4, 6, 11) or 10 ml. (no. 6) of the alkyl halide was added. Except where stated the yields were 90-100%. All products were recrystallised from acetone/ethanol.

1. A solution of triphenylethylphosphonium tribromomercurate(II) in acetone and methyl iodide was refluxed. After heating for 15 min., the initially colourless solution had become bright yellow. Evaporation of the solvent gave a residue of triphenylethylphosphonium tri-iodomercurate(II), m.p. 127-127.5°, mixed m.p. 127.5-128° (Found: C, 28.0; H, 2.8%).

2. The same reaction occurred when a similar solution was kept at 25° for 1 hr. Triphenylethylphosphonium tri-iodomercurate(II) was obtained, m.p. 127.5-128°, mixed m.p. 128° (Found: C, 27.9; H, 2.6%).

3. The tribromomercurate was converted to the tri-iodomercurate, m.p. <u>ca</u>. 120° (Found: C, 27.3; H, 2.3%) on refluxing with ethyl iodide for 1 hr.

4. Triphenylmethylphosphonium dibromo-iodomercurate(II) reacted with methyl iodide in acetone in 1 hr. at 25° to give triphenylmethylphosphonium tri-iodomercurate(II), m.p. and mixed m.p. 146.5° (Found: C, 26.45; H, 2.3%).

5. Triphenylethylphosphonium dibromo-iodomercurate(II) was converted to the tri-iodomercurate, m.p. <u>ca</u>. 120° (Found: C, 27.3; H, 2.4%) on refluxing with ethyl iodide for 1 hr.

6. Triphenylmethylphosphonium bromodi-iodomercurate(II) was converted to the tri-iodomercurate, m.p. 146°, mixed m.p. 146-146.5° (Found: C, 26.3; H, 2.2%) by refluxing with methyl iodide for 2½ hr.

7. Triphenylethylphosphonium bromodi-iodomercurate(II) reacted with methyl iodide in acetone in 1 hr. at 25° to give triphenylethylphosphonium tri-iodomercurate(II), m.p. 127.5-128°, mixed m.p. 128°

(Found: C, 27.5; H, 2.4%).

8. The bromodi-iodomercurate also reacted with ethyl iodide on refluxing for 1 hr. to give the tri-iodomercurate, m.p. *ca.* 120° (Found: C, 27.6; H, 2.5%).

9. Triphenylmethylphosphonium tri-iodomercurate(II) (0.21 g.) was refluxed with ethyl bromide in acetone for 2 hr. and allowed to stand for 10 hr. at room temperature. The volatiles were removed "in vacuo" and 0.20 g. of a yellow solid, m.p. 143.5° was obtained. On crystallisation from acetone/ethanol the first fraction had m.p. 143.5-144° (Found: C, 27.3; H, 2.5; I, 38.5; Br, 4.6%), the second had m.p. 143.5-144° (Found: C, 27.0; H, 2.7; I, 38.9; Br, 4.3%) (Calc. for $Ph_3PMeHgI_3$: C, 26.5; H, 2.1; I, 44.4%; calc. for $Ph_3PMeHgBrI_2$: C, 28.1; H, 2.2; I, 31.3; Br, 9.9%). The ultraviolet spectrum in methanol of the first fraction in the region 2400-3200 A shows features intermediate between the spectra of $[Ph_3PMe][HgBrI_2]$ and $[Ph_3PMe][HgI_3]$ (Fig. 4.1).

10. Triphenylmethylphosphonium tri-iodomercurate(II) was refluxed with excess *n*-butyl bromide for 4 hr. Partial solution of the complex occurred. On cooling pale yellow crystals of triphenylmethylphosphonium bromodi-iodomercurate(II) were obtained, m.p. 140°, mixed m.p. 139-140° (Found: C, 27.8; H, 2.2%).

11. A solution of triphenylethylphosphonium tri-iodomercurate(II) (0.14 g.) in acetone and ethyl bromide was maintained at 25° for 1 hr. No colour change was observed. When the solvents were removed "in vacuo", the complex was recovered unchanged, m.p. 127-127.5°, mixed m.p. 128-128.5° (Found: C, 27.6; H, 2.6%).

Reaction of Mercuric Bromide with Methyl Iodide.

1. Mercuric bromide was refluxed with excess methyl iodide for 10 hr. A yellow residue was obtained after removal of the methyl iodide by distillation. Impure bromoiodomercury(II) was partly separated from unreacted mercuric bromide by ether extraction, recrystallised from the same solvent and obtained as a yellow microcrystalline powder still impure, m.p. 212-214° (lit.[23] 229°) (Found: Hg, 50.2; Br, 24.7; I, 24.8. Calc. for HgBrI: Hg, 49.2; Br, 19.6; I, 31.2%).

2. A solution of mercuric bromide (0.184 g.) in acetone and methyl iodide (10 ml. and 5 ml. respectively) was maintained at 25° for 1 hr. When the solvents were removed "in vacuo" the residual solid (0.186 g.) showed only a faint yellow colouration, hence very little halogen exchange occurred.

Reaction of Mercuric Iodide with n-Butyl Bromide.

Mercuric iodide (0.70 g.) was refluxed with *n*-butyl bromide (30 ml.). The mercuric iodide slowly dissolved. Initially a pink solution was obtained, which deepened in colour on continued heating. After 4 hr. the solution was black in colour. The reaction mixture yielded black crystals on standing for 24 hr. at 0°. These contained iodine, and partly dissolved on heating with aqueous potassium iodide. The resultant solution yielded precipitates with aqueous solutions of quaternary iodides, its behaviour being similar to that of K_2HgI_4.

Reactions of Quaternary Halides with Alkyl Halides.

In all reactions *ca*. 5% of ethanol (v/v) was added to the system to increase the solubility of the quaternary halide. The yields were near quantitative (> 90%) and all products were recrystallized from ether/ethanol.

1. Triphenylethylphosphonium bromide was converted to the iodide, m.p. 166.5-167°, mixed m.p. 166-166.5° (Found: C, 57.0; H, 5.0%), by refluxing with ethyl iodide in acetone for 1 hr.

2. A solution of triphenylethylphosphonium bromide (0.14 g.) in acetone (10 ml.) and methyl iodide (5 ml.) was maintained at 25° for 1 hr. Triphenylethylphosphonium iodide, m.p. 166.5°, mixed m.p. 166-166.5° (Found: C, 57.3; H, 4.8%) was obtained.

3. A solution of triphenylethylphosphonium iodide (0.11 g.) in acetone (10 ml.) and ethyl bromide (5 ml.) was maintained at 25° for 1 hr. Triphenylethylphosphonium bromide, m.p. and mixed m.p. 203-204° (Found: C, 64.6; H, 5.5%) was obtained.

(b) Reactions of Halo(triphenylphosphine)cadmium(II) Complexes. Preparation of Dihalobis(triphenylphosphine)cadmium(II) Complexes.

The complexes were precipitated on mixing ethanol solutions containing the stoichiometric amounts of the cadmium halide and triphenylphosphine.

1. Di-iodobis(triphenylphosphine)cadmium(II).- Fine white needles, m.p. 241.5-242° (lit.[18] 243°, with preliminary softening) (Found: C, 48.45; H, 3.6. Calc. for $C_{36}H_{30}CdI_2P_2$: C, 48.5; H, 3.4%).

2. Dibromobis(triphenylphosphine)cadmium(II).- Recrystallized from ethanol, white needles, m.p. 225-226° (lit.[18] 225-226°) (Found: C, 54.3; H, 4.1. Calc. for $C_{36}H_{30}Br_2CdP_2$: C, 54.2; H, 3.8%). The same complex was precipitated, m.p. 224-225°, mixed m.p. 225-226° (recrystallized from ethanol) (Found: C, 54.7; H, 3.9%), in an attempt to prepare the complex ($Ph_3P.CdBr_2$) by mixing ethanol solutions of the stoichiometric amounts of triphenylphosphine and $CdBr_2.4H_2O$.

Preparation of Bis(triphenylalkylphosphonium) tetrahalocadmate(II) Complexes.

1. Bis(triphenylmethylphosphonium) tetraiodocadmate(II) was precipitated on mixing stoichiometric amounts of cadmium iodide and triphenylmethylphosphonium iodide in ethanol solution, and, recrystallized from acetone, had m.p. 173.5-174° (Found: C, 39.9; H, 3.55; Cd, 9.6; I, 40.6. $C_{38}H_{36}CdI_4P_2$ requires C, 38.8; H, 3.1; I, 43.3; Cd, 9.6%). The complex was only sparingly soluble in boiling acetone and less soluble in ethanol and was difficult to purify.

Bis(triphenylethylphosphonium) tetrabromocadmate(II) was similarly prepared and recrystallized from ethanol, m.p. 108.5-109° (Found: C, 46.8; H, 4.3. $C_{40}H_{40}Br_4CdP_2$ requires C, 47.3; H, 3.9%). Triphenylmethylphosphonium tri-iodocadmate(II) could not be prepared by reaction between the stoichiometric amounts of the tetraiodocadmate and cadmium iodide in acetone. Crystallization from the resultant solution gave the tetraiodocadmate unchanged.

Reactions of Dihalobis(triphenylphosphine)cadmium(II) Complexes With Alkyl Halides.

With Methyl Iodide.

The complexes $(Ph_3P)_2CdX_2$ (where X is Br or I) were refluxed with methyl iodide, either alone or in the presence of an added solvent. Details are given in Table 5.2. In experiments 1, 4, 25 ml. of methyl iodide were used, in 2, 5, 6, 20 ml. of both methyl iodide and acetone were used, and in 3, 7, 10 ml. of both methyl iodide and ethanol were used. After the reactions the solvents were evaporated to dryness giving a pale brown residue in each case. In expts. 1, 3, 7 the total

TABLE 5.2

Reaction of $(Ph_3P)_2CdX_2$ (where X is Br, I) with Methyl Iodide

Expt.	Complex	w_1	t	w_2	w_3	Product		Found	
						m.p.	mixed m.p.	%C	%H
1	$(Ph_3P)_2CdI_2$	0.35	1	0.50	0.42	173.5–174	173–174	40.4	3.7
2	"	0.54	1	0.76	0.72	173–174	173.5–174	40.1	3.6
3	"	0.34	1	0.48	0.45	173.5–174	173.5–174	39.6	3.6
4	$(Ph_3P)_2CdBr_2$	0.32	1	0.40	0.48	162–164	–	40.2	3.7*
5	"	0.54	2	0.82	0.80	166	–	–	–
6	"	0.52	1	0.80	0.77	170.5–171.5	171.5–172.5	40.2	3.7
7	"	0.58	1	0.89	0.85	166	–	40.1	3.7

w_1 wt. reactant complex.

w_2 wt. product (see text).

w_3 theoretical wt. product (for $[Ph_3PMe]_2CdI_4$ alone).

t reaction time (hr); for added solvents see text.

* Found also: I, 39.6; Br, 1.8.

weight of product is given (w_2). In nos. 2, 5, 6, 5 ml. of ethanol were added to the residue. The weight of the insoluble fraction, white crystals, is given (w_2). Further solid ca. 0.01-0.02 g. (pale brown) was obtained on evaporation of the ethanol. In expt. 4, 5 ml. of acetone was added and the insoluble fraction weighed (w_2). In each instance the product contained a small amount of an ether soluble fraction, which was shown (expts. 5, 7) to contain free iodine and another component. The bulk of the product (w_2) in each experiment was recrystallised to constant m.p. from acetone or acetone/ethanol, and is considered to be primarily bis(triphenylmethylphosphonium) tetraiodocadmate(II) (m.p. and mixed m.p.'s given in Table 5.2). As in most instances the weight of crude products exceeded that required for the formation of the tetraiodocadmate(II) alone, and as it was not possible to purify the product adequately by recrystallization,* a number of reactions were attempted to characterise unequivocally the quaternary cation formed.

An attempt was made to precipitate the cadmium iodide in the product as $(Ph_3P)_2CdI_2$, and thus liberate the quaternary iodide, by decomposition of the product with excess triphenylphosphine. The method was similar to that successfully used with the iodomercurate complexes (Section 5.3). However precipitation was incomplete. Similarly an attempt to precipitate the cadmium iodide as $(dipy)CdI_2$, by decomposition with excess 2,2'-dipyridyl was unsuccessful.

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* In expt. 4 this was probably due to the presence of a small amount of the reactant complex, which has similar solubility properties to the product, as is indicated by the microanalyses of the product (Table 5.2).

Satisfactory characterization was achieved by reaction of the product in acetone with 2 moles of mercuric iodide/mole of product (assumed to be $[Ph_3PMe]_2CdI_4$), when triphenylmethylphosphonium tri-iodomercurate(II) was crystallized in > 80% yield, on the addition of ethanol to lower the solubility. The method was used to characterize the product from reactions 2, 3, 5, 7. The tri-iodomercurate was recrystallized from acetone/ethanol, giving the following results:

Expt.	M.p.	mixed m.p.	Found	
			C%	H%
2	146-146.5	146.5-147	26.3	2.1
3	146-146.5	146-146.5	26.7	2.4
5	147	146.5-147	26.5	2.2
7	146.5	146.5	26.6	2.1

The infra-red spectra of the crude tetraiodocadmate from reaction 4, and the purified product from reaction 7 were compared with the spectrum of authentic bis(triphenylmethylphosphonium) tetraiodocadmate(II), and were found to be essentially identical.

The following experiments were performed to attempt to elucidate what reaction competes with the major reaction.

1. Triphenylphosphine (0.43 g.) was refluxed with acetone (40 ml.) for 15 hr. It was recovered unchanged, m.p. 79.5-80° (lit.[24] 79°), mixed m.p. (with original) 80.5-81°. The ultra-violet spectrum of the unpurified product in methanol did not differ appreciably from that of the reactant; in particular the product had a maximum at 2580-2600 A, $\varepsilon_{max} = 1.1 \times 10^4$, the reactant had a maximum at 2600 A, $\varepsilon_{max} = 1.1 \times 10^4$. The spectrum of triphenylphosphine in methanol is very similar to that in ethanol.[25]

2. Bis(triphenylmethylphosphonium) tetraiodocadmate(II) (0.30 g.) was refluxed with methyl iodide (10 ml.) in acetone (20 ml.) for 5 hr. Evaporation of the solvent and addition of 3 ml. of ethanol gave an insoluble fraction (0.28 g.) of bis(triphenylmethylphosphonium) tetraiodocadmate(II), recrystallised from acetone, m.p. 172-173°, mixed m.p. 173-174° (Found: C, 39.8; H, 3.7%), with an infra-red spectrum identical to that of authentic $(Ph_3PMe)_2CdI_4$. Evaporation of the ethanol gave *ca.* 0.01-0.02 g. of pale brown solid. Extraction with ether gave an insoluble fraction, white crystals, presumably the tetraiodocadmate, and a trace of brown soluble material, not iodine.

With Ethyl Bromide.

1. $(Ph_3P)_2CdBr_2$ (0.91 g., 1.14 mmole) was refluxed with ethyl bromide (20 ml.) in acetone (20 ml.). After 5 hr. heating, all the complex had dissolved and after 10 hr. precipitation of product began. This was filtered off after 12½ hr., and consisted of bis(triphenylethylphosphonium) tetrabromocadmate(II) (0.52 g., 0.51 mmole, 45%), recrystallised from ethanol, m.p. 108.5-109.5°, mixed m.p. 109-109.5° (Found: C, 47.3; H, 4.4%). The filtrate was evaporated and gave 0.56 g. of white solid. This had m.p. 130-155° (Found: C, 50.15; H, 4.1%), after two recrystallizations from ethanol, and is probably a mixture of reactant and product.

2. $(Ph_3P)_2CdI_2$ (0.93 g., 1.05 mmole) was similarly reacted with ethyl bromide in acetone. Solution of the complex was complete in 6 hr., and precipitation of the product commenced after 10 hr. This was filtered off after 14 hr. and consisted of bis(triphenylethylphosphonium) tetrabromocadmate(II) (0.57 g., 0.56 mmole, 53%), recrystallised from

ethanol, m.p. 107.5–108°, mixed m.p. 108° (Found: C, 47.0; H, 4.4%). The filtrate was evaporated and gave 0.39 g. of white solid. This gave bis(triphenylethylphosphonium) tetrabromocadmate(II), m.p. 105–106.5°, mixed m.p. 107–107.5° (Found: C, 46.9; H, 4.2%), on recrystallization from ethanol. The mother liquor was evaporated, and gave a cream glue, which was iodine free.

<u>Reactions Using Shorter Time.</u>

1. $(Ph_3P)_2CdBr_2$ (0.47 g.) was refluxed with ethyl bromide in acetone (20 ml. of each) for 10½ hr. Evaporation to dryness gave 0.50 g. of white solid, recrystallised from acetone/ethanol, m.p. 145° (with preliminary softening), which could not be separated into recognisable components on further recrystallization. The mother liquor from the original recrystallization yielded bis(triphenylethylphosphonium) tetrabromocadmate(II), m.p. and mixed m.p. 108.5–109° (Found: C, 46.8; H, 4.3%).

2. $(Ph_3P)_2CdI_2$ (0.74 g.) was similarly refluxed with ethyl bromide in acetone for 11 hr. The solid obtained on evaporation (0.73 g.) gave bis(triphenylethylphosphonium) tetrabromocadmate(II), m.p. 107.5–108° (ethanol twice), mixed m.p. 108–109.5° (Found: C, 46.2; H, 4.4%) – still impure – as the first fraction on crystallisation from ethanol, and white crystals, m.p. <u>ca</u>. 140° as the second fraction.

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SECTION B

CHAPTERS 6 - 8

SOME REACTIONS OF GROUP VB ORGANO-METALLOIDAL COMPOUNDS

CHAPTER 6

A Review of the Reactions of Group VB Organometalloidal Compounds with Haloalkanes

In this review some general types of reactions of trivalent Group VB organometalloidal compounds are considered. The account is not intended to be exhaustive.

(1) Reactions with Monohaloalkanes.

The trialkyls of nitrogen, phosphorus, arsenic, and antimony react with alkyl halides to form quaternary halides, e.g.

$$Me_3P + MeI \longrightarrow [Me_4P]I.$$

Triarylphosphines and -arsines also give quaternary halides with alkyl halides, but triphenylamine fails to react.[1] Stibines containing more than one aromatic group are not quaternized by methyl iodide.[2] Reaction between triphenylstibine and methyl iodide at elevated temperatures gives triphenylstibine di-iodide, iodobenzene, and ethane.[3] Bismuth trialkyls undergo cleavage reactions with alkyl halides,[4] e.g.,

$$Me_3Bi + 2MeI \xrightarrow{200^\circ} MeBiI_2 + 2C_2H_6.$$

Radical exchange occurs in a number of quaternization reactions. Thus the reaction, $Et.\mathit{n}Pr.\mathit{i}BuN + 2MeI \longrightarrow [Me_2.\mathit{i}Bu.\mathit{n}PrN]I + EtI$, was observed instead of the expected formation of $[Me.Et.\mathit{i}Bu.\mathit{n}PrN]I$.[5]

(2) Reactions with Dihaloalkanes.

Methylene dibromide and ethylene dibromide react with trimethylamine to give either a mono- or a di-quaternary bromide,[6] e.g.,

$$Me_3N + CH_2Br_2 \longrightarrow [Me_3NCH_2Br]Br$$
$$2Me_3N + CH_2Br_2 \longrightarrow [Me_3NCH_2NMe_3]Br_2.$$

The formation of trimethylbromomethylammonium bromide proceeds more readily than its conversion to the diquaternary compound, which has been attributed to the inductive effect of the Me_3N^+ group. Similarly the reaction between ethylene dibromide and phenyldimethylphosphine yields two products,[7] which may best be formulated as $[PhMe_2P(CH_2)_2Br]Br$ and $[PhMe_2P(CH_2)_2PMe_2Ph]Br_2$. Only the diquaternary compounds have been isolated in the reactions of methylene di-iodide and ethylene dibromide with triphenylphosphine.[8]

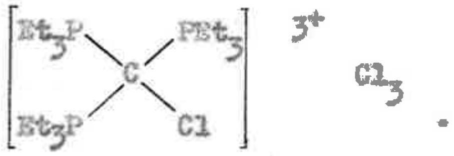
(3) Reactions with Trihaloalkanes.

In the presence of air bromoform reacts with trimethylamine or triethylamine with the formation of the corresponding trialkylammonium bromide, but no reaction could be achieved with chloroform.[9] Iodoform can form compounds with a number of amines,[10] e.g., with primary amines the compounds $RNH_2.CHI_3$, $(RNH_2)_2.CHI_3$, and $(RNH_2)_3.CHI_3$ are known. The structures of these compounds are not known, but may be related to those of the amine:CCl_3I adducts (see below). Triphenylphosphine reacts with bromoform under conditions favourable for a free radical reaction to yield triphenyldibromomethylphosphonium bromide, the following mechanism being proposed,[11]

$$CHBr_3 \longrightarrow CHBr_2^{\bullet} + Br$$
$$Ph_3P + {}^{\bullet}CH_2Br \longrightarrow Ph_3P^{\bullet}CHBr_2$$
$$Ph_3P^{\bullet}CHBr_2 + CHBr_3 \longrightarrow [Ph_3PCHBr_2]Br + CHBr_2^{\bullet}.$$

(4) Reactions with Perhaloalkanes.

Dehn[12] found that a number of amines (both aliphatic and aromatic) react with carbon tetrabromide to form adducts of varying stoichiometries, e.g., $Py(CBr_4)_2$. The structures of these compounds are not known. When the reactions were not performed under rigorously anhydrous conditions the hydrobromide of the base was obtained. Trimethylamine and carbon tetrabromide react in the presence of oxygen to give an unidentified crystalline solid and formaldehyde,[9] but carbon tetrachloride does not react. It has been observed that a number of amines react with carbon tetrachloride under pressure in the absence of air at ca. 200° to form coloured resinous materials. These were frequently hygroscopic and, when leached with water, gave an extract containing ionic chloride.[13] Hantzsch and Hibbert[14] reported that triethylphosphine and carbon tetrachloride react readily to form the compound $(Et_3P)_3CCl_4$, which is considered to have the structure,[15]



Trimethylphosphine and carbon tetrachloride do not react at room temperature, but at 150° a tarry mass is obtained.[13]

Trichloroiodomethane reacts with a wide variety of Group VB organometalloidal compounds in the absence of air[13,16] to give adducts of the type, $R_3M.ICCl_3$ (where M is N, P, As, Sb). In Table 6.1 the compounds investigated are classified.

Considerable evidence was obtained to show that the products were non-ionic, and that a coordinate bond is formed between the metalloid and iodine, thus, $R_3M \longrightarrow ICCl_3$. When M is P, As the bonding may be stabilized by back coordination, and the unexpected stability

TABLE 6.1

Behaviour of Group VB Organometalloidal Compounds with Trichloroiodomethane

1:1 Complex formed	No reaction
Me_2NH, Me_3N, Et_3N, $PhNH_2$, Ph_3P, Me_3P, Me_3As, Ph_3As, Me_3Sb.	$MeNH_2$, en, Py, Ph_3N, Ph_3Sb.

of the compound $Ph_3P.ICCl_3$ has been explained in this way. Reactions of the type

$$R_3M + R_3M'.ICCl_3 \longrightarrow R_3M' + R_3M.ICCl_3$$

were attempted but did not proceed to completion. Thus trimethylamine partially displaces trimethylphosphine from its adduct with CCl_3I, while trimethylphosphine partially displaces trimethylamine from its adduct.

Trifluoroiodomethane reacts with trimethylphosphine, -arsine, and -stibine with the formation of trifluoromethyldimethyl metalloidal compounds and the corresponding tetramethylquaternary iodide. These reactions are termed radical exchange reactions.

$$2Me_3M + CF_3I \longrightarrow CF_3MMe_2 + [Me_4M]I \quad \text{(where M is P, As, Sb).}^{17}$$

A trace of fluoroform is also obtained. However the reaction with trimethylamine yields a considerable amount of fluoroform, tetramethylammonium iodide, and an unidentified white solid shown to contain C-F bonds. A plausible intermediate in the reaction with trimethylphosphine is the quaternary iodide $[Me_3PCF_3]I$.[17] This may be synthesised by the reaction $CF_3PMe_2 + MeI \longrightarrow [Me_3PCF_3]I$, and is stable at room temperature. As it was not detected in the reaction between trimethylphosphine and trifluoroiodomethane (in the absence of an added solvent), any reaction scheme proposed must be such as to remove it completely. The following observations[17] are relevant in deciding the mechanism.

(a) Trimethyltrifluoromethylphosphonium iodide is obtained mixed with tetramethylphosphonium iodide when trimethylphosphine and trifluoroiodomethane react in carbon tetrachloride. Its isolation in this reaction can be attributed to its insolubility in the solvent used.

(b) Trimethyltrifluoromethylphosphonium iodide is soluble in liquid trifluoroiodomethane at room temperature and is recovered unchanged on evaporation of the solvent.

(c) Tetramethylphosphonium iodide is soluble in liquid trifluoroiodomethane and can be recovered unchanged.

(d) Trimethyltrifluoromethylphosphonium iodide is insoluble in trimethylphosphine and not even traces of tetramethylphosphonium iodide are formed, but with added ethanol some tetramethylphosphonium iodide is obtained.

It thus appears that solvent effects play an important part in the reaction and that trifluoroiodomethane may be regarded as the solvent. The ready solubility of trimethyltrifluoromethylphosphonium iodide in this compound explains why the reaction proceeds to completion in trifluoroiodomethane and not in carbon tetrachloride.[17] The results of a qualitative investigation of the solvent properties of liquid trifluoroiodomethane are given in Chapter 7.

Removal of the trimethyltrifluoromethylphosphonium iodide in the reaction between trifluoroiodomethane and trimethylphosphine could occur by one of two mechanisms:[17]

(a) Dissociation of the quaternary iodide to trifluoromethyldimethylphosphine and methyl iodide and reaction of the latter with trimethylphosphine.

$$[Me_3PCF_3]I \longrightarrow Me_2PCF_3 \ + \ (MeI \xrightarrow{Me_3P} [Me_4P]I).$$

In view of the stability of the trifluoromethyl quaternary compound such a mechanism seems unlikely.

(b) Nucleophilic attack of trimethylphosphine on a methyl group of the quaternary ion,

$$Me_3P\colon \ + \ Me - PMe_2CF_3^{\,+} \longrightarrow Me_4P^+ \ + \ Me_2PCF_3.$$

The formation of trimethyltrifluoromethylphosphonium iodide is considered[17] to occur via nucleophilic attack of trimethylphosphine on the relatively positive iodine of trifluoroiodomethane,

$$Me_3P\colon \ + \ \overset{\delta+}{I} - \overset{\delta-}{CF_3} \longrightarrow [Me_3PI]^+CF_3^-,$$

followed by a rearrangement of the trimethyliodophosphonium compound through a pentacovalent state to trimethyltrifluoromethylphosphonium iodide. A similar pentacovalent intermediate has been postulated in the reaction of triphenylphosphine with bromomethylcyanide.[18] The polarization of trifluoroiodomethane may be inferred from a comparison of its alkaline hydrolysis and its reaction with methyl-lithium with the corresponding reactions of methyl iodide,[17,19] e.g.,

$$OH^- \ + \ ICF_3 \longrightarrow HOI \ + \ (CF_3^- \xrightarrow{\text{solvent}} CF_3H)$$

$$OH^- \ + \ MeI \longrightarrow MeOH \ + \ I^-$$

$$\text{and} \quad MeLi \ + \ ICF_3 \longrightarrow MeI \ + \ LiCF_3$$

$$MeLi \ + \ MeI \longrightarrow C_2H_6 \ + \ LiI.$$

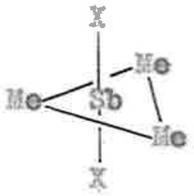
The small amount of fluoroform produced in the reactions of the compounds Me_3M (where M is P, As, Sb) with trifluoroiodomethane can be attributed to a side reaction in which the trifluoromethyl anion of the compound $[Me_3PI]^+[CF_3]^-$ attacks a neighbouring molecule abstracting hydrogen.[17] The low yield of fluoroform indicates that the change,

$$[Me_3PI]^+CF_3^- \longrightarrow \begin{array}{c}\text{pentacovalent}\\ \text{state}\end{array} \longrightarrow [Me_3PCF_3]^+I^-$$

is rapid. The far greater yield of fluoroform in the reaction between trimethylamine and trifluoroiodomethane can be related to the inability of nitrogen to form a pentacovalent state. Thus $[Me_3NI]^+CF_3^-$ cannot rearrange to $[Me_3NCF_3]^+I^-$, and all the CF_3^- formed is available for hydrogen abstraction.

The reactions of other Group VB organometalloidal compounds with trifluoroiodomethane have been studied and the results are presented in Chapter 7.

Independent evidence as to the existence of quaternary cations of the type R_3MI^+ (where M is N, P, As, Sb) is conflicting. Wells has shown that the trimethylantimony dihalides have a trigonal bypyramidal structure,[20]



(where X is Cl, Br, I).

Both antimony-halogen bond distances are the same length, which eliminates the structure $[Me_3SbX]^+X^-$. The structure is best regarded as being intermediate between the pentacovalent state and the ionic $[Me_3Sb]^{2+}X_2^-$.[20]

It has been recently shown that a number of tertiary phosphine di-iodides have conductances similar to those of 1:1 electrolytes in nitrobenzene,[21] and it is considered that these compounds have the structure $[R_3PI]^+I^-$. Derivatives of the R_3PI^+ cations with uni-negative, complex metal halide anions were also prepared, e.g. tricyclohexyliodophosphonium tri-iodomercurate(II) $[(\underline{cyclo}\text{-}C_6H_{11})_3PI]^+[HgI_3]^-$. These compounds also behave as 1:1 electrolytes in nitrobenzene.[21]

The conductivities of a number of tertiary phosphine dibromides and dichlorides were found to decrease with time. This was considered to be due to the conversion of the initially ionic compounds to the pentacovalent state.[21] Derivatives of the cations R_3PX^+ (where X is Cl, Br) with uni-negative, complex metal halide anions have also been isolated, the conductances of which do not vary with time and are of similar magnitude to those of 1:1 electrolytes.

Recently similar evidence has been advanced to show that the tertiary arsine dihalides have a similar ionic constitution.[13,22] Hantzsch[23] suggested that the 1:1 addition compounds formed between amines and halogens were ionic, $[R_3NX]^+X^-$ (where X = Cl, Br, I). However, recent X-ray studies[24] have shown that the compounds have a linear arrangement of the nitrogen and iodine atoms, N-I-I, the bonding being essentially covalent. An ionic compound with the stoichiometry $Py.2I_2$ can be isolated in the reaction between pyridine and iodine. It has the structure $[Py_2I]^+I_7^-$.[25]

The results of some recent studies of reactions of Group VB organometalloidal compounds with trifluoroiodomethane, carried out by other workers,[26,27] are considered during the presentation of the original work in Chapter 7.

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CHAPTER 7

The Reactions of Some Group VB Organometalloidal Compounds with Trifluoroiodomethane, and the Solvent Properties of Trifluoroiodomethane

In the previous chapter (p. 157) the reactions between the Group VB trimethyls and trifluoroiodomethane[1] were considered. In this chapter the results of some exploratory investigations of the reactions of other Group VB organometalloidal compounds with trifluoroiodomethane are discussed. In general these reactions have proved to be more complex than those of the trimethyls. Their investigation is at this stage incomplete, and any conclusions that are drawn are tentative. An outline of further experiments that would assist in understanding these reactions is given in this chapter.

1. The Reaction of Triphenylphosphine with Trifluoroiodomethane.

Triphenylphosphine and trifluoroiodomethane do not react at room temperature, nor is reaction detectable after heating the reactants for 24 hr. at 160°. Some reaction may be achieved by heating for longer times at 160°, while the reaction proceeds more readily at 170°. Some details of several experiments are given in Table 7.1.

The volatiles after reaction consisted primarily of unreacted trifluoroiodomethane. However it was shown by vapour phase chromatography that traces of two more volatile compounds were present. One was identified as fluoroform by infra-red spectroscopy. The other was possibly hexafluoroethane.

The major product of the reaction was an involatile yellow glue-like substance, which could be partly crystallized by the addition

TABLE 7.1

The Reaction of Triphenylphosphine with Trifluoroiodomethane

Expt.	Ph_3P (mmole)	CF_3I^i (mmole)	Temp. (°C)	Time (hr.)	CF_3I^r (mmole)	Other volatiles* (g.)	Mole ratio**
1	2.1	6.6	160	24	6.6	-	-
2	3.1	8.6	160	40	7.9	0.02	0.2_2
3	3.5	9.5	160 173	40 26	6.4	0.04	0.8_9
4	2.8	6.2	173	70	3.8	0.03	0.8_6
5	3.8	11.8	158 170	22 27	9.0	0.05	0.7_4
6	3.7	10.9	172	46	7.1	0.06	1.0_3

i, initial.

r, recovered, at -131° on distillation of the volatiles (see Chapter 8).

* As obtained at -196° " " " " " " " "

** Mole ratio of CF_3I reacted : Ph_3P initial.

of benzene. This substance must contain almost all of the trifluoromethyl groups and the iodine of the trifluoroiodomethane consumed in the reaction.

It is proposed that the yellow substance consists of a mixture of triphenylphosphonium iodide, $[Ph_3PH]I$, trifluoromethylated triphenylphosphonium iodides, e.g., $[CF_3.C_6H_4.PPh_2H]I$ and compounds with further trifluoromethyl substitution, and trifluoromethylated triphenylphosphines. The positions of the trifluoromethyl groups in the aromatic rings are considered with the discussion of the reaction mechanism. In the following discussion the observed properties of the reaction product are considered with reference to the proposed constitution.

The mole ratios of trifluoroiodomethane consumed : triphenylphosphine used in the various experiments (Table 7.1) are approximately equal to the average number of trifluoromethyl groups present per Ph_3P unit in the product, since only a trace of trifluoromethyl containing volatiles was formed in the reaction. The ratios are slightly high as they are calculated on the basis of the trifluoroiodomethane recovered at -131°, and a small amount of trifluoroiodomethane was present in the volatiles recovered at -196°.

The yellow glue obtained in the reaction had the following properties:

(1) It was slightly soluble in cold water with some decomposition. The aqueous extract contained ionic iodide, and gave precipitates with aqueous sodium tetraphenylborate, and with potassium tetraiodomercurate(II), suggesting that a quaternary iodide was present.

(2) The product was soluble in acetone, and it was possible to dissolve a considerable amount of mercuric iodide in the resultant solution. This is also evidence for the presence of a quaternary iodide, as mercuric iodide is only sparingly soluble in cold acetone, but has a high solubility in the presence of a quaternary iodide due to complex formation (Chapter 5, section 5.2). Crystals could not be obtained from the acetone solution.

(3) Fluoroform was not obtained when the product was decomposed with aqueous base, even on warming, hence the product cannot contain $P-CF_3$ bonds, which yield fluoroform with aqueous base at room temperature.[2] It may therefore be concluded that the trifluoromethyl groups of the trifluoroiodomethane consumed in the reaction are present in the aromatic groups of the product. Thus the reaction does not yield phenyltrifluoromethylphosphines, and the course of the reaction between triphenylphosphine and trifluoroiodomethane is not the same as the corresponding reaction of trimethylphosphine. Phenylbistrifluoromethylphosphine has recently been prepared by the reaction between phosphorobenzene, $(PhP)_4$, and trifluoroiodomethane.[3]

(4) The infra-red absorption bands of the product are given in Table 7.2. The product was examined as a Nujol mull in the region 667-1400 cm^{-1}, and in chloroform solution in the region 830-2500 cm^{-1}. In the overlapping region the resolution obtained was greater for the chloroform solution, and some weak bands were observed that could not be detected in Nujol. The infra-red absorption bands of triphenylphosphonium iodide,[4] and the principal bands of benzotrifluoride[5] are also given in Table 7.2. If, as suggested, the product contains $CF_3.C_6H_4-$

TABLE 7.2

The Infra-red Absorption Bands of the Product from the Reaction between Triphenylphosphine and Trifluoroiodomethane, together with Those of Triphenylphosphonium Iodide[4] and Benzotrifluoride.[5]

Reaction Product[a]	Reaction Product[b]	$[Ph_3PH]I$[c]	$C_6H_5.CF_3$[d]
2439(w)			
ca. 2220(w,b)			
1587(m)			
1480(m)			
1437(vs)			1460 1428(vs)
1330(ms)	1316(w)		1328(vs)
1170(ms)	1159(m)	1184 1166(w)	1178 1155(vs)
1125(vs)	1114(s)	1120(vs)	1130(vs)
1066(w)			1073(vs)
1030(w)		1040 1015(mw) 1002 988	1030(vs)
1000(m)			
971(m)			
ca. 909(w)	930(w)	930(s)	927(vs)
	877(w)	880(m)	
	761(m)	771(s)	769(vs)
	747(m)	756(m)	
	735 727(s) 710	744 735(vs)	
		720(s)	
	690(s,b)	698 692(vs) 683	695(vs)

Maxima are given in $cm.^{-1}$.

Intensities: (s) strong, (m) medium, (w) weak, (b) broad, (v) very.

The intensities are not strictly comparable, as the spectra were obtained using different conditions.

a. Measured in chloroform solution.
b. Measured as a Nujol mull.
c. Measured as a Nujol mull (from 625-1300 cm^{-1}).
d. Measured in the liquid phase; only the most intense bands are given.

groups, absorption bands should be found in similar positions to those of benzotrifluoride.

It is evident from Table 7.2 that, for almost every band in the spectrum of the reaction product, there is a band (or group of bands) of triphenylphosphonium iodide or benzotrifluoride with a closely corresponding position. The pair of bands of triphenylphosphonium iodide[4] at 930 and 880 cm^{-1} appear in the spectrum of the reaction product in Nujol, but are absent in the spectrum in chloroform. This pair of bands appear in different positions in the spectra of other triphenylphosphonium salts,[4] and it is therefore likely that their position would change with a change of medium. The band of the reaction product at 2439 cm^{-1} may be attributed to a P-H stretching vibration, which gives weak bands in the region 2350-2440 cm^{-1}.[6] The band at 1587 cm^{-1} is due to a C=C vibration of the phenyl groups.[7]

(5) When the reaction product was decomposed with aqueous base, an oily product was obtained, which, on reaction with excess mercuric iodide, gave white crystals, which were separated into di-μ-iododi-iodobis(triphenylphosphine)dimercury(II) (Chapter 5, section 5.3), and another compound (or a mixture of compounds) with a similar spectrum, but having in addition bands characteristic of CF_3-phenyl bonds.[8]

(6) The yellow colour of the product slowly changed to a cream-brown on exposure to the air, the substance being slightly hygroscopic. Triphenylphosphonium iodide is white and is not hygroscopic when pure.[4] The colour may, however, be explained by the presence of traces of phosphorus tri-iodide or compounds containing P-I bonds.

The analogous reaction of triphenylarsine with trifluoroiodomethane at 240° yields arsenic tri-iodide as a major product.[9] Thus it is possible that the reaction with triphenylphosphine at 170° yields traces of phosphorus tri-iodide or phenyliodophosphines, which would account for both the colour and the slightly hygroscopic nature of the product. In addition some iodine may be formed in the reaction, which would give coloured polyiodide anions with the iodide anions formed.

The Mechanism of the Reaction.

It is considered that the reaction between triphenylphosphine and trifluoroiodomethane proceeds by a free radical mechanism, since it is known that trifluoroiodomethane undergoes homolytic fission on heating.[10] In addition it has been shown that the reaction may be induced by ultra-violet radiation.

The following steps are proposed in the reaction:

Initiation

$$CF_3I \rightleftharpoons CF_3^{\bullet} + I^{\bullet} \qquad 7.1$$

$$CF_3^{\bullet} + Ph_3P \rightleftharpoons CF_3{\cdot}C_6H_5{\cdot}PPh_2^{\bullet} \qquad 7.2$$

The free radical $CF_3{\cdot}C_6H_5{\cdot}PPh_2^{\bullet}$ is henceforth termed $X^{\bullet}$.

Propagation

$$CF_3I + X^{\bullet} \longrightarrow XI + CF_3^{\bullet} \qquad 7.3$$

$$XI \longrightarrow CF_3{\cdot}C_6H_4{\cdot}PPh_2 + HI \qquad 7.4$$

$$\text{or} \quad CF_3I + X^{\bullet} \longrightarrow CF_3{\cdot}C_6H_4{\cdot}PPh_2 + HI + CF_3^{\bullet} \qquad 7.5$$

Quaternisation

$$Ph_3P + HI \longrightarrow [Ph_3PH]I \qquad 7.6$$

$$CF_3{\cdot}C_6H_4{\cdot}PPh_2 + HI \longrightarrow [CF_3{\cdot}C_6H_4{\cdot}PPh_2H]I \qquad 7.7$$

Termination

$$CF_3^{\bullet} + CF_3^{\bullet} \longrightarrow C_2F_6 \qquad 7.8$$

Iodine atoms may be removed by the reaction,

$$X^{\bullet} + I^{\bullet} \longrightarrow CF_3.C_6H_4.PPh_2 + HI \text{ etc.} \qquad 7.9$$

or by $Z + I^{\bullet} + I^{\bullet} \longrightarrow I_2$ (where Z is a third body) 7.10

The iodine would be removed as a polyiodide anion.

Fluoroform may be produced by the reaction,

$$X^{\bullet} + CF_3^{\bullet} \longrightarrow CF_3.C_6H_4.PPh_2 + CF_3H \qquad 7.11$$

Further substitution to give bis(trifluoromethyl) substituted compounds would follow a similar pattern. It must be noted that when the average number of trifluoromethyl groups per Ph_3P unit equals one, all the phosphorus atoms present must be in the quaternary state (provided reactions 7.3-7.7 proceed essentially to completion). Any further trifluoromethyl substitution would probably be accompanied by the formation of free hydrogen iodide. In the present experiments the average number of trifluoromethyl groups per Ph_3P unit did not exceed approximately one (Table 7.1, and p. 166).

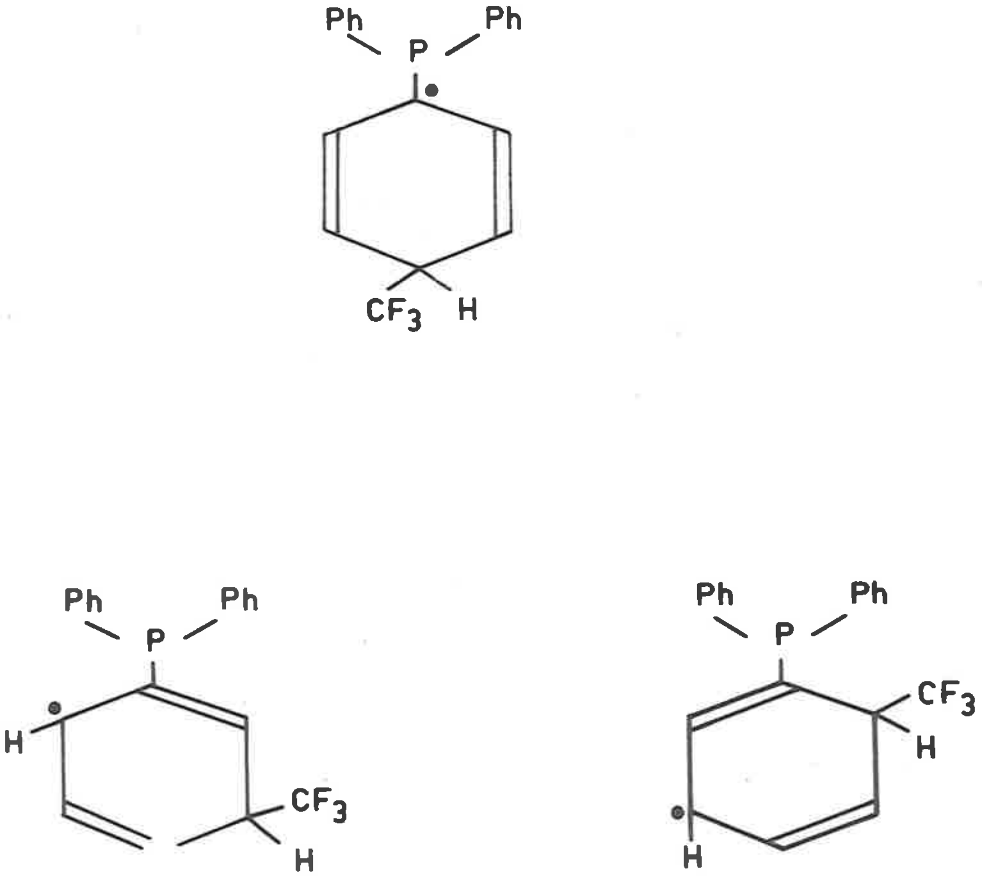
The various steps in the mechanism are now to be considered in detail. Reaction 7.1 has been discussed (see above). The C-I bond dissociation energy is 57 kcal.[11]

Reactions similar to 7.2 have been shown to occur. Charles and Whittle[12] have studied the reactions of trifluoromethyl radicals with aromatic hydrocarbons, and have shown that most of the trifluoromethyl groups do not abstract hydrogen with the formation of fluoroform, but add to the aromatic rings forming substituted cyclohexadienyl radicals analogous to $X^{\bullet}$. All three possible positions of the phenyl rings in triphenylphosphine are likely to be attacked by the trifluoromethyl radicals. If there is any conjugation of the phosphorus atom with the aromatic rings, this would favour ortho and para attack. However, the ortho position is sterically hindered, and there are two meta positions to each para position. Probably these effects are insufficient to prevent substitution in all three positions. Some possible structures for X* are given in Fig. 7.1.

An approximate heat of formation of the radical X* can be given by subtraction of the bond dissociation energy of the CF_3-C bond from the sum of the resonance energy of the phenyl ring and the dissociation energy of a π bond of a Kekulé structure of the phenyl ring. In the absence of bond dissociation data for compounds closely related to X*, the CF_3-C bond dissociation energy may be considered approximately equal to that of C-C bond of CF_3-CH_3, viz., 90 kcal.[11] The resonance energy of the phenyl ring would be approximately equal to that of benzene, viz., 36 kcal.[13] Similarly the dissociation energy of a π bond of a Kekulé structure of the phenyl group would be approximately equal to that of benzene. This is approximately equal to the dissociation energy of a π bond of cyclohexene, which, calculated from the enthalpy of hydrogenation of this compound,[14] is 65 kcal. Using this data the heat of formation of X* is _ca._ 10 kcal.

It is not possible to decide whether propagation would proceed by the two step process, reactions 7.3 and 7.4, or by the single step 7.5. Overall both processes are the same and the heat of the overall reaction is equal to the sum of the bond dissociation energies of CF_3-I and of a C-H bond of the radical X* less the sum of the bond dissociation energies of H-I and of a π bond of a Kekulé structure

FIG. 7.1 SOME POSSIBLE STRUCTURES FOR THE FREE RADICAL $CF_3 \cdot C_6H_5 \cdot PPh_2 \cdot$



of the trifluoromethylated phenyl group formed and the resonance energy of the same group. Using similar approximations to those used to calculate the heat of formation of X$^{\bullet}$, the heat of reaction 7.5 is ca. -10 kcal. The heats of reactions 7.3 and 7.4 are ca. 4 and -14 kcal. respectively.

Of the quaternisation reactions, 7.6 and 7.7, reaction 7.6 is initially favoured on statistical grounds. It is also favoured electronically, as trifluoromethyl substitution of a phenyl group of triphenylphosphine would enhance delocalization of the phosphorus lone pair due to the inductive effect of the trifluoromethyl group. Once all free triphenylphosphine has been quaternised further substitution must occur either in the phenyl rings of triphenylphosphonium iodide, or in the aromatic groups of the trifluoromethylated compounds.

Some evidence for reaction 7.8 has been obtained in that a trace of a very volatile compound other than trifluoroiodomethane and fluoroform was obtained in the reaction. It may be noted that this reaction is the termination step in the reaction of trifluoromethyl radicals with aromatic hydrocarbons.[12]

While the formation of fluoroform by reaction 7.11 would be energetically favourable (The reaction has been calculated to be exothermic to the extent of ca. 100 kcal.), it requires interaction between two free radicals both of which would be in low concentration. Thus the yield of fluoroform is low. A similar reaction has been postulated to account for the formation of fluoroform in the reaction between aromatic hydrocarbons and trifluoromethyl radicals.[12] Formation of fluoroform by the reaction,

$$CF_3I + X^{\bullet} \longrightarrow CF_3.C_6H_4.PPh_2 + CF_3H + I^{\bullet}$$

is relatively unlikely due to the screening of the carbon atom of CF_3I by the attached atoms.

In the reaction between trifluoromethyl radicals and aromatic hydrocarbons, the ultimate fate of the trifluoromethylated cyclohexadienyl radicals (related to $X^{\bullet}$) was considered to be dimerization. The infra-red spectrum of the product had a band at 1670 cm^{-1}, which was considered due to an olefinic double bond.[12] Dimerization of $X^{\bullet}$ would be unlikely in the reaction between triphenylphosphine and trifluoroiodomethane as it requires interaction between two free radicals which would be in low concentration, whereas the postulated scheme for the removal of $X^{\bullet}$ (reactions 7.3 and 7.4, or reaction 7.5) requires interaction between $X^{\bullet}$ and trifluoroiodomethane, which is present in excess. In addition the orientation of the free radicals for dimerisation would be impeded by the viscous solvent sheath, initially of triphenylphosphine and then of reaction product. There was no evidence for the presence of an olefinic double bond in the infra-red spectrum of the reaction product.

The reaction between benzene and trifluoroiodomethane may be useful in deciding whether the foregoing explanation of the reaction between triphenylphosphine and trifluoroiodomethane is correct. It is conceivable that steps analogous to 7.2-7.5 could occur in the reaction between benzene and trifluoroiodomethane. However, reactions analogous to 7.6 and 7.7 are clearly impossible. Thus if this reaction between trifluoroiodomethane and triphenylphosphine has been correctly interpreted, the reaction between benzene and trifluoroiodomethane may yield free hydrogen iodide.

A study of the reaction between di-iodobis(triphenylphosphine)-mercury(II) and trifluoroiodomethane would also be useful. Although the presence of the mercuric iodide would impede the reaction between triphenylphosphine and trifluoroiodomethane, it would convert quaternary iodide formed to an iodomercurate, which may be more stable and more readily crystallised than the reaction product obtained in its absence. A preliminary experiment has shown that this reaction does occur, though it is much slower than the reaction of the free phosphine. $(Ph_3P)_2HgI_2$ is insoluble in liquid trifluoroiodomethane. After prolonged heating of these reactants at ca. 180°, the white reactant complex is converted to a yellow substance, which is soluble in liquid trifluoroiodomethane, and is probably an iodomercurate complex. Further work is intended on this reaction.

It is also intended to study the reaction between triphenylphosphine oxide and trifluoroiodomethane. If this follows a similar pattern to that of triphenylphosphine, it should lead to the formation of a mixture of triphenylhydroxyphosphonium iodide and analogous compounds with trifluoromethyl substitution in the phenyl rings. These compounds should be sufficiently stable to identify.

2. The Reaction of Triphenylarsine with Trifluoroiodomethane.

A preliminary study of this reaction at 160° was carried out. Heating for 28 hr. gave a yellow glue, which consisted largely of unreacted triphenylarsine together with a small amount of a yellow solid which fumed in the air, and may contain As-I bonds. Cullen[9] has recently reported a detailed examination of this reaction at 240°, when fluoroform, benzene, benzotrifluoride, and arsenic tri-iodide were formed, together with an involatile yellow oil which was not identified. The reaction did not yield any phenyltrifluoromethylarsines. These, however, were prepared by the reaction between phenylhaloarsines and trifluoroiodomethane in the presence of mercury.[9]

3. The Reaction of Phenyldimethylamine with Trifluoroiodomethane.

Phenyldimethylamine and trifluoroiodomethane do not react at temperatures below 170°, but reaction may be effected by prolonged heating at 180°. The volatiles after reaction consisted of unreacted trifluoroiodomethane and fluoroform. Some details of a typical experiment are given in Table 7.3. There is no obvious stoichiometric relationship between the amount of trifluoroiodomethane or phenyldimethylamine used and the amount of fluoroform evolved. In another similar experiment the reactants were heated for a longer time, but there was no significant increase in the amount of fluoroform produced.

The major product of the reaction was an orange-brown slightly hygroscopic solid. The substance contains the elements C, H, N, F, I, but no formula is readily evident from the analytical data (Chapter 8). The composition varies slightly with different preparations, but this may be due to the difficulty of purifying the product. It is sparingly soluble in water, ethanol, acetone, chloroform, benzene, and glacial acetic acid, giving a yellow solution in each solvent, but it cannot be recrystallized from any of these solvents. In most solvents the undissolved solid becomes oily. The substance is partly decomposed by warm water. The aqueous solution contains iodide ions, and gives a milky precipitate with aqueous potassium tetraiodomercurate(II), suggesting the presence of quaternary

TABLE 7.3

The Reaction of Phenyldimethylamine with Trifluoroiodomethane

$PhMe_2N$ (mmole)	CF_3I^i (mmole)	Temp. (°C)	Time (hr.)	CF_3I^r (mmole)	CF_3H^* (mmole)
7.9	13.1	180	67	8.4	2.1

i, initial.

r, recovered at −131°, on distillation of the volatiles (see Chapter 8).

*, recovered at −196°, on distillation of the volatiles (see Chapter 8).

TABLE 7.4

Infra-red Absorption Bands of the Product from the Reaction between Trifluoroiodomethane and Phenyldimethylamine

The maxima are given in cm^{-1}; the intensities are in parentheses.

3425 (w)	1170 (w)	946 (m)
2653 (m)	1127 (s)	896 (m)
1605 (s)	1063 (s)	820 (m,b)
1511 (s)	1019 (w)	719 (vs, vb)
1266 (w)	990 (m)	693 (vs, vb)

Abbreviations for intensities are as in Table 7.2.

ammonium groups in the product. The product reacts with mercuric iodide in acetone solution, but the iodomercurate complex formed cannot be readily crystallised. The substance is more soluble in concentrated hydrochloric acid than in water, suggesting the presence of free amine groups. This is also indicated by the N:I ratio of the product, which is *ca.* 1·7:1. The product is decomposed by aqueous base with the formation of an oily residue.

It seems likely that the product of the reaction between trifluoroiodomethane and phenyldimethylamine is polymeric or is a mixture of several compounds. It does not have a sharp melting point, but softens, swells, and decomposes on heating.

The infra-red spectrum of the compound was obtained in the region 667-2500 cm^{-1}, and the absorption bands are given in Table 7.4. The compound was examined as a Nujol mull. (The regions in which the C-H stretching and deformation vibrations occur, which are hidden by the Nujol absorption, were not examined, as these frequencies would not greatly assist in determining the nature of the product.).

The band at 2653 cm^{-1} indicates the presence of a $\overset{+}{\mathrm{N}}$-H bond in the product. The $\overset{+}{\mathrm{N}}$-H stretching vibration of trimethylammonium iodide gives rise to a band at 2725 cm^{-1}.[15] The bands at 1605 cm^{-1} and 1511 cm^{-1} are probably due to aromatic C=C vibrations.[7] There do not appear to be any olefinic double bonds present in the product. The maxima at 1170 and 1127 cm^{-1} are probably due to the presence of trifluoromethyl groups,[8] substituted in the aromatic rings. The bands at 1063 and 1019 cm^{-1} may be due to methyl rocking vibrations, which give rise to bands at 1052 and 1020 cm^{-1} in the spectrum of trimethylammonium iodide.[15] It is possible, however, that absorption associated with C-F bonds also contributes to the maximum at 1063 cm^{-1}. For most of the bands in the region 800-1000 cm^{-1} there are bands at similar positions in the spectrum of trimethylammonium iodide,[15] suggesting the presence of quaternary ammonium groups (with methyl substituents) in the product. The intense absorption shown in the region 667-800 cm^{-1} may be attributed to substitution in the aromatic groups.[16]

The ultra-violet spectrum of the product in ethanol shows the following features: (1) a broad band at ca. 2550 A, (2) a slight inflexion between 2800 and 3000 A, (3) a very broad and shallow maximum at ca. 3500 A, and (4) the absorption tails into the visible region, becoming negligible at ca. 5000 A. The origins of the effects (1) and (2) may be similar to those of the maxima of phenyldimethylamine, which occur at 2500 and 2960 A.[17] The tailing of the absorption into the visible could be due to the presence of small amounts of coloured compounds. However, it was noticeable that treatment of the product with various solvents failed to change its colour. The cause of (3) is not known. It is not due to an azo group, which has a characteristic absorption at ca. 4300 A.[18]

Mechanism of the Reaction.

Because of the uncertainty as to the nature of the product no detailed mechanism can be given. All that can be done is to indicate how the detected functional groups could be produced. The formation of CF_3-aryl groups, $\overset{+}{N}$-H bonds, and iodide ions can be attributed to a process similar to the mechanism proposed for the reaction of triphenylphosphine with trifluoroiodomethane. The yield of fluoroform was much lower in this reaction than in that between phenyldimethylamine and trifluoroiodomethane. Since the reactions were carried out using similar conditions, it is unlikely that a process analogous to 7.11 would account for the formation of the major amount of the fluoroform obtained in the reaction of phenyldimethylamine. It is probable that hydrogen abstraction occurs from methyl groups, e.g.,

$$CF_3^{\bullet} + Me_2NPh \longrightarrow CF_3H + PhNMeCH_2^{\bullet} .$$

There are a number of possibilities for the removal of the $PhNMeCH_2^{\bullet}$ radicals, e.g., dimerisation, or substitution in the aromatic rings. However, it is possible that some would react with trifluoroiodomethane,

$$PhNMeCH_2^{\bullet} + ICF_3 \longrightarrow PhNMeCH_2I + CF_3^{\bullet},$$

and the phenylmethyliodomethylamine formed could then react with a further amount of amine, e.g.,

$$PhNMeCH_2I + PhNMe_2 \longrightarrow [PhNMeCH_2NMe_2Ph]I.$$

Such a process would account for the apparent presence of free amine groups in the product.

If the product is a polymer, it is not easy to explain how it would be formed. It is to be noted, however, that the reaction between trifluoromethyl radicals and benzene[12] gave a polymeric solid besides the products mentioned previously.

Because of the complexity of the system it is doubtful whether a further study of the reaction would be profitable. If the product is polymeric, X-ray diffraction would probably be the only satisfactory method of establishing the structure. It may be useful to degrade this substance with aqueous base, and attempt to characterize the amines formed. A molecular weight determination would probably be meaningless unless further information as to the structure could be obtained.

4. Reaction of Phenyldimethylphosphine with Trifluoroiodomethane.

In contrast to the previous reactions it is possible to obtain a crystalline derivative of the major product of this reaction. However, due to an ambiguity in the results so far obtained, the course of the reaction is not yet understood.

Trifluoroiodomethane and phenyldimethylphosphine do not react at room temperature, but reaction occurs readily in 7 hr. at ca. 95°. Some details of several experiments are given in Table 7.5. The volatiles after reaction consisted of unreacted trifluoroiodomethane and fluoroform. The amount of fluoroform obtained is not significantly affected by prolonged heating. Approximately two-thirds of the trifluoromethyl radicals of the trifluoroiodomethane consumed in the reaction appear as fluoroform.

The major product of the reaction is a pale-yellow semi-solid substance, which could not be crystallised and appeared to decompose slightly on exposure to the air. Reaction of this substance with mercuric iodide in acetone gave yellow crystals with the analytical composition, $C_{16}H_{21}P_2Hg_2I_5$ (F nil). This compound is henceforth referred to as Y. There must be at least one other compound in the crude product besides the one that gives rise to Y, as some trifluoromethyl groups of the trifluoroiodomethane consumed in the reaction must be present in this material.

A plausible structure for Y is $[\mathrm{PhMe}\underset{\substack{\downarrow \\ \mathrm{HgI_2}}}{\mathrm{P}}\mathrm{CH_2PMe_2Ph}][\mathrm{HgI_3}]$, the compound being derived from phenylmethylphosphinomethylphenyldimethylphosphonium iodide, $[\mathrm{PhMePCH_2PMe_2Ph}]\mathrm{I}$. An analogous compound, diphenylphosphinomethyltriphenylphosphonium bromide, has recently been

TABLE 7.5

The Reaction of Phenyldimethylphosphine with Trifluoroiodomethane

Expt.	$PhMe_2P$ (mmole)	CF_3I^i (mmole)	Temp. (°C)	Time (hr.)	CF_3I^r (mmole)	CF_3H^* (mmole)
1	7.0	13.0	105	76	7.0	4.3
2	7.0	13.2	94	7	7.9	3.7
3	7.0	11.7	94	11	6.4	4.0

i, initial

r, recovered at −131° on distillation of the volatiles.

*, recovered at −196° on distillation of the volatiles.

prepared by the reaction between triphenylphosphinemethylene and diphenylbromophosphine.[19]

$$Ph_3P{=}CH_2 \;+\; Ph_2PBr \longrightarrow [Ph_3PCH_2PPh_2]Br.$$

This compound could not be crystallized but various crystalline derivatives were obtained. With mercuric bromide it gave a derivative for which the structure, $[Ph_2\underset{\displaystyle HgBr_2}{\overset{}{\underset{\downarrow}{P}}}CH_2PPh_3][HgBr_3]$, was proposed. This is analogous to that proposed for Y.

The ultra-violet spectrum of the compound Y showed maxima at 2600 and 3000 A, which are characteristic of the tri-iodomercurate ion (Chapter 3, pp. 58,59). The infra-red absorption bands of this compound are given in Table 7.6, and the complete spectrum in Fig. 7.2.

If the structure proposed for compound Y is correct, then it follows from the reactions discussed in Chapter 4 that Y should react with methyl iodide to yield methylenebis(phenyldimethylphosphonium tri-iodomercurate(II))*, $[PhMe_2PCH_2PMe_2Ph][HgI_3]_2$ ($C_{17}H_{24}P_2Hg_2I_6$). When compound Y was reacted with methyl iodide a compound with analytical composition, $C_{17}H_{24}P_2Hg_2I_6$, (henceforth referred to as Z), was obtained. However, the analytical data agree quite well with the compound being phenyltrimethylphosphonium tri-iodomercurate(II) ($C_9H_{14}PHgI_3$). The ultra-violet spectrum of Z shows maxima at 2600 and 3000 A, characteristic of the tri-iodomercurate ion. The infra-red spectrum of this compound is given in Fig. 7.3, and the absorption bands in Table 7.6. It is evident that the infra-red spectrum of

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* The terminology is that of Chemical Abstracts.

TABLE 7.6

Infra-red Absorption Bands of Derivatives of the Product of the Reaction between Phenyldimethylphosphine and Trifluoroiodomethane, and of Phenyltrimethylphosphonium iodide.

The maxima are given in cm^{-1}. The compounds were examined as Nujol and hexachlorobutadiene mulls.

Y	Z	PhMe$_3$PI
1754(w)	1754(w)	1666(w,b)
1626(w)	1608(w)	1589(w)
1439(m)	1431(m)	1440(s)
1408 1395 (m)	1389(m)	1404(w)
1364(m)		1342(w)
1323(mw)	1330 1312 (m)	1314(w)
1305(mw)		1298 1290 (w-m)
1196(w)		
1174(w)	1176(w)	1156(w-m)
1136 1124 (m-s) 1109	1152(w)	
	1133(s)	1129(s) 1109(ms)
		1035(w)
957 939 917 (s-vs) 897	952(vs)	971(vs)
	917 909 (vs)	918(w)
876 870 (s)	877(m)	883(ms) 876(s)
812(s)	855(w)	
	824(m)	840(w)
780(m) 771(s)	787(w) 775(m)	773(m)
		746(vs)
743 737 (vs)	753(vs)	725(m)
717(m)		687(vs)
	709(vw,b)	
704(w)		
687(vs)	686(vs)	

Abbreviations for intensities are as in Table 7.2.

Fig. 7.2. The Infra-red Spectrum of the Compound Y.

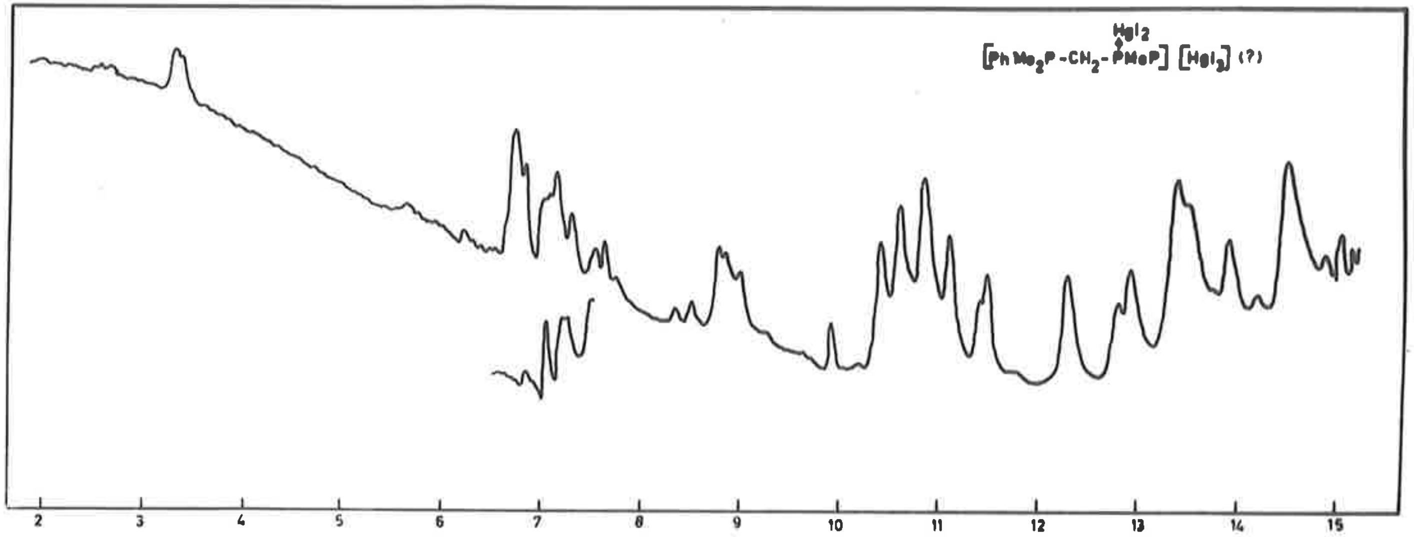
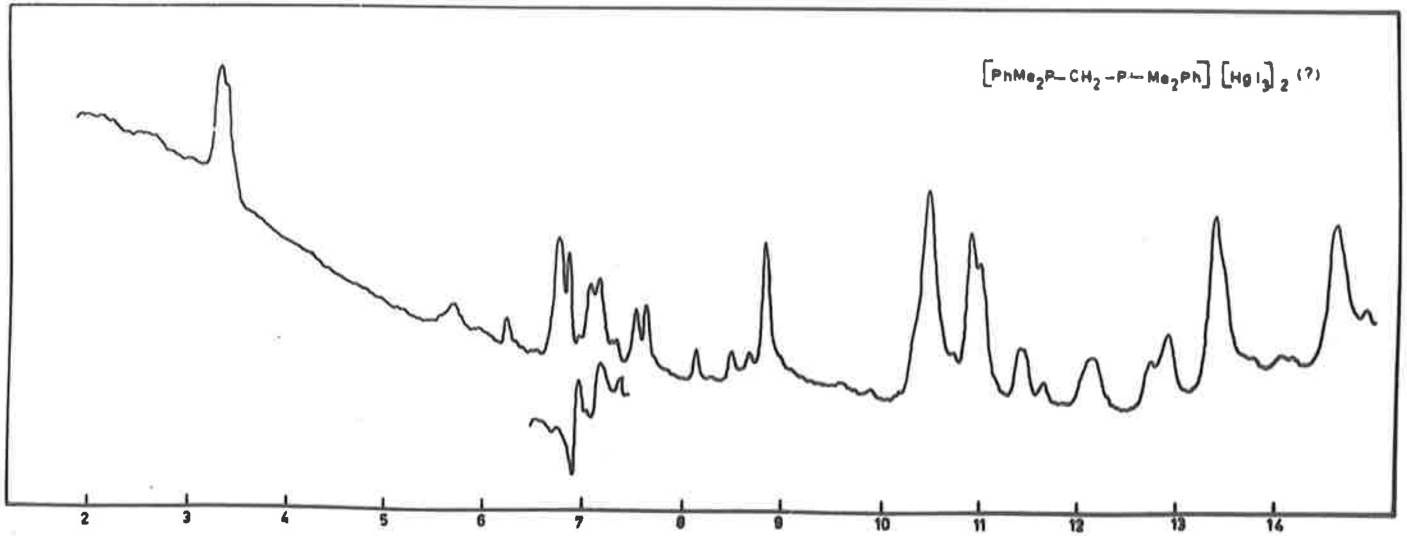


Fig. 7.3. The Infra-red Spectrum of the Compound Z.



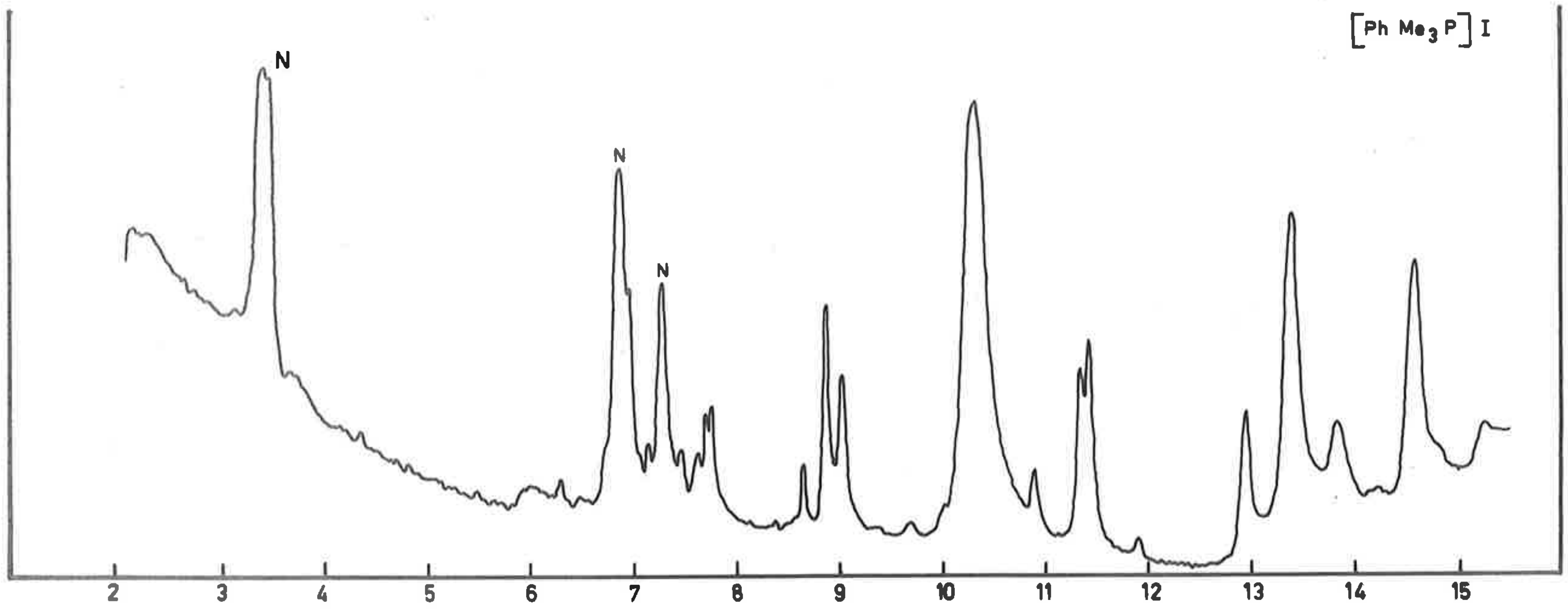
this compound differs significantly from that of phenyltrimethylphosphonium iodide, Fig. 7.4 (the absorption bands are given in Table 7.6). In Chapter 2 it was shown that the infra-red spectra of tetramethylphosphonium iodide and its iodomercurate derivatives were very similar in the 667-2500 cm^{-1} region, hence it would not be expected that the infra-red spectrum of trimethylphenylphosphonium tri-iodomercurate(II) would differ so markedly from that of phenyltrimethylphosphonium iodide.

However, when the compound Z was decomposed with excess triphenylphosphine (using the method of Chapter 5, section 5.3), the quaternary iodide liberated had analytical composition, melting point, and infra-red spectrum corresponding to phenyltrimethylphosphonium iodide. The amount of $(Ph_3P)_2HgI_2$ precipitated in the reaction corresponded nearly exactly to that required if Z was $C_{17}H_{24}P_2Hg_2I_6$, but also agrees reasonably with Z being phenyltrimethylphosphonium tri-iodomercurate(II).

Thus there is an apparent contradiction in the experimental results. If Z is $[PhMe_2PCH_2PMe_2Ph](HgI_3)_2$ the formation of phenyltrimethylphosphonium iodide in the decomposition reaction with triphenylphosphine is difficult to understand, unless rupture of a P-C bond occurs. If Z is phenyltrimethylphosphonium tri-iodomercurate(II) the pronounced difference in its infra-red spectrum from that of phenyltrimethylphosphonium iodide remains to be explained, and it is difficult to account for Y.

The formation of phenyltrimethylphosphonium iodide in the reaction between phenyldimethylphosphine and trifluoroiodomethane would be expected if the reaction proceeds according to the equation,

Fig. 7.4. The Infra-red Spectrum of Phenyltrimethylphosphonium Iodide.



$$2PhMe_2P + CF_3I \longrightarrow PhMeCF_3P + [PhPMe_3]I.$$

The reaction would thus be similar to those of the Group VB trimethyls with trifluoroiodomethane. However, both infra-red and analytical evidence show that Y cannot be $[PhMe_3P][HgI_3]$. In addition this reaction would not account for the high yield of fluoroform.

If compound Y is $[\underset{\underset{HgI_2}{\downarrow}}{PhMeP}CH_2PMe_2Ph][HgI_3]$, the formation of phenylmethylphosphinomethylphenyldimethylphosphonium iodide in the reaction between phenyldimethylphosphine and trifluoroiodomethane could be attributed to the reaction sequence,

$$CF_3I \rightleftharpoons CF_3^{\bullet} + I^{\bullet}$$

$$CF_3^{\bullet} + PhMe_2P \longrightarrow CF_3H + PhMePCH_2^{\bullet}$$

$$PhMePCH_2^{\bullet} + CF_3I \longrightarrow PhMePCH_2I + CF_3^{\bullet}$$

$$PhMePCH_2I + PhMe_2P \longrightarrow [PhMePCH_2PMe_2Ph]I\ .$$

It is evident that further study of this reaction is required. The following related experiments would also be useful.

(1) An authentic sample of phenyltrimethylphosphonium tri-iodomercurate(II) must be synthesized.

(2) The compound $[PhMe_2PCH_2PMe_2Ph]I_2$ can probably be prepared by the reaction,

$$2PhMe_2P + CH_2I_2 \longrightarrow [PhMe_2PCH_2PMe_2Ph]I_2.$$

From this compound an authentic sample of methylenebis(phenyldimethylphosphonium tri-iodomercurate(II)) can be prepared, and its decomposition by triphenylphosphine can be studied.

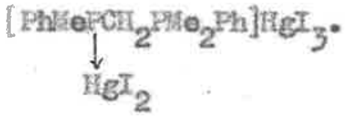
These iodomercurate complexes would provide reliable standards for the identification of the compound Z by infra-red spectroscopy.

(3) Reaction of the complex $(PhMe_2P.HgI_2)_2$ with trifluoroiodomethane would enable the compound Y to be prepared readily in a single reaction.

(4) Independent verification of whether Y is the mercuric iodide derivative of phenylmethylphosphinomethylphenyldimethylphosphonium iodide may be possible. It may be possible to prepare $[PhMePCH_2PMe_2Ph]I$ by reaction between phenyldimethylphosphinemethylene and methylphenyliodophosphine,

$$PhMe_2P{=}CH_2 \quad + \quad PhMePI \longrightarrow [PhMe_2PCH_2PMePh]I.$$

However, phenylmethyliodophosphine has not yet been prepared, and may not exist. Phenylmethylbromophosphine is known, from which it would be possible to prepare $[PhMe_2PCH_2PMePh]Br$ by a similar procedure. This latter compound could then be treated with a solution of mercuric iodide in alcoholic potassium iodide, and this reaction should give



$$[PhMe\underset{\substack{\downarrow \\ HgI_2}}{P}CH_2PMe_2Ph]HgI_3.$$

By contrast with the reaction between phenyldimethylphosphine and trifluoroiodomethane, phenyldimethylarsine fails to react at 100°, but at 170° reaction occurs yielding $PhCF_3$, CF_3H, MeI, $MeAs(CF_3)_2$, $PhAs(CF_3)_2$, $PhAs(Me)CF_3$, and $PhAs(CH_3)_3I_3$.[20]

It is evident that the direct reaction between trifluoroiodomethane and phenyl containing phosphines and arsines does not provide a satisfactory method for the preparation of phenyltrifluoromethyl-phosphines and -arsines. These compounds can, however, be obtained by methods recently developed by Clark[3] and Cullen[9] (see pp. 167 and 176).

5. Solvent Properties of Trifluoroiodomethane.

As has previously been discussed (Chapter 6, p. 159), the hydrolysis of trifluoroiodomethane, and its reaction with methyl lithium is consistent with the polarization of the molecules being $\overset{\delta +}{\mathrm{I}}\text{———}\overset{\delta -}{\mathrm{CF_3}}$.[1,21] Though the ionization of this compound is low (conductivity $< 10^{-9}$ ohm^{-1} at -45°),[21] the ionization $CF_3I \rightleftharpoons I^+ + CF_3^-$ has been postulated as a step in the exchange reaction between trifluoroiodomethane and labelled sodium iodide in ethanol.[21] A qualitative study of solubilities in liquid trifluoroiodomethane was therefore undertaken as a preliminary to examining whether trifluoroiodomethane would function as an ionising solvent. The results of the solubility studies were also of interest in connection with the postulation of a specific solvent effect associated with trifluoroiodomethane in the radical exchange reactions between this compound and the Group VB trialkyls[1] (Chapter 6, p. 157). Haszeldine and West[1] found that liquid trifluoroiodomethane dissolved both trimethyltrifluoromethylphosphonium iodide and tetramethylphosphonium iodide in appreciable amounts, suggesting that this compound may show unusual solvent properties for a perhaloalkane. Recently it has been argued that ionization of trifluoroiodomethane does not occur in the iodide exchange reaction, else the formation of fluoroform would occur, due to hydrogen abstraction by CF_3^- from the solvent used.[22] Accordingly the present study has not been continued beyond the study of the qualitative solubilities.

The solubility of most compounds was very low at temperatures lower than the boiling point of trifluoroiodomethane (-22.5),[23] hence most compounds were investigated at room temperature (ca. 20°), by sealing the solute with trifluoroiodomethane in Carius tubes. The results are summarized in Table 7.7. Compounds classified as soluble have solubilities greater than ca. 1% (weight/vol.); those as sparingly soluble have detectable solubilities but < 1%.

In general the results are as would be expected for a perhaloalkane. Thus a solution of iodine in trifluoroiodomethane is coloured violet, as is its solution in carbon tetrachloride. The appreciable solubility of a number of quaternary iodides appears anomalous. In this regard trifluoroiodomethane resembles methyl iodide, which is known to dissolve a number of quaternary iodides. A chemical similarity between the methyl and the trifluoromethyl group is of course suggested by the radical exchange reactions.[1]

An unusual feature of the tetramethylphosphonium iodide/trifluoroiodomethane system is the formation of two layers at room temperature. With the particular amounts of the compounds used in the present experiments, this two layer system was found to change to a one layer system, on cooling to ca. -3°. The lower layer of the two layer system was generally found to have a yellow colour. The intensity of the colour could be considerably reduced by trap to trap distillation of the trifluoroiodomethane immediately before use. It is therefore likely that the colour is due to the presence of iodine, formed by photochemical decomposition of trifluoroiodomethane. This would give coloured periodides in the presence of the quaternary iodide, e.g., $I^- + I_2 \rightleftharpoons I_3^-$.

The striking difference between the solubilities of tetra-

TABLE 7.7

Solubilities in Liquid Trifluoroiodomethane

	Soluble		Sparingly soluble	Insoluble	
-78°			$[Me_4P]I$		
-45°	$[Me_4P]I$	ICN		$[PyH][HgI_3]$	SbF_3
				$[PyH]_2[Hg_3I_8]$	HgI_2
				$[Me_4N]I$	
ca.-20°	$[Me_4P]I$*	Ph_3P	I_2	LiCl	$CrCl_3$
	$[Ph_3PMe]I$**	Ph_3As	AsI_3	KI	Cu_2I_2
	$[Ph_3AsMe]I$**	Ph_3Sb	SnI_4	$[Me_4N]I$	$PhAs(O)(OH)_2$
		$(PhCH_2)_2S_2$		$[PH_4]I$	SbI_3
	$[CF_3PMe_3]I$	$(C_5H_5)_2Fe$		$[NH_3(OH)]Cl$	$BiCl_3$
	NOCl	ICl_3	$(PhNH)_2CO$	PCl_5	$PhCH_2CO_2H$
	PCl_3	ICN		$[Me_4P][HgI_3]$	
	Me_2S	Ph_3PO_4		$[Me_4P][Hg_2I_5]$	
	$PhNMe_2$			$[PyH]_2[HgI_4]$	
	$PhPMe_2$			$[PyH]_2[Hg_3I_8]$	
				$[NH_4][BF_4]$	
				$[Ni(NH_3)_6]BF_4$	
				Co(II) Salen	
				$[pNO_2\text{-}C_6H_4N_2]BF_4$	

* Two layer system, see text.

** Single layer system.

methylammonium iodide and tetramethylphosphonium iodide is difficult to explain. As has already been discussed, the size of the two cations is very similar, and the conductances of the corresponding tri-iodomercurates in acetone are virtually identical at the same concentration (Chapter 3, p. 74). It is tempting to suggest that solvation of the phosphonium compound is in some way related to the fact that phosphorus possesses d orbitals in its valence shell, whereas nitrogen does not, but this leaves the insolubility of phosphonium iodide unexplained.

When tetramethyl-ammonium or -phosphonium iodide is heated with trifluoroiodomethane radical exchange does not occur. The reactants are recovered essentially unchanged, though traces of free iodine and possibly of hexafluoroethane were obtained, presumably from decomposition of the trifluoroiodomethane. The failure to observe radical exchange in these systems is in agreement with the mechanism proposed for radical exchange between the Group VB trimethyls and trifluoroiodomethane (Chapter 6, p. 157). This requires as an initial step the nucleophilic attack of the trimethyl on the relatively positive iodine of trifluoroiodomethane. With the tetramethyl compounds such a nucleophilic attack is not possible.

The solubility studies do provide additional evidence that trifluoroiodomethane does not ionize, $CF_3I \rightleftharpoons CF_3^- + I^+$. Such ionization should enable solvolysis of compounds such as antimony trifluoride to occur, e.g.,

$$CF_3I + SbF_3 \longrightarrow I^+[SbF_3CF_3]^-,$$

which would probably enable the compounds to dissolve. However, such compounds were generally insoluble and no evidence of reaction was obtained.

Watterson[24] has found that trifluoroiodomethane and cobaltocene react with the formation of a red oil, which has been identified as π-cyclopentadienyl(1-endo-trifluoromethylcyclopentadiene)cobalt. The other product was probably cobalticenium iodide.

$$2Co(C_5H_5)_2 + CF_3I \longrightarrow [Co(C_5H_5)_2]^+I^- + C_5H_5(CF_3.C_5H_5)Co$$

Ferrocene does not react similarly even on heating for 110 hr. at 130°.

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CHAPTER 8

Experimental

1. General Technique.

A conventional Pyrex glass vacuum system[1,2,3] was used for the manipulation of volatile compounds. These were purified by "trap to trap" distillation, by means of suitable slush baths. The molecular weights of volatile compounds were obtained by the Regnault method. The reactions with trifluoroiodomethane were carried out in sealed Carius tubes (Dreadnought glass) of 40-60 ml. capacity, air and moisture being excluded. The reaction mixtures were heated in a Carius furnace. Where necessary compounds were handled in an atmosphere of oxygen free,dry nitrogen.

Microanalyses.

Except where stated, all analyses were by the C.S.I.R.O. Microanalytical Laboratories, Melbourne.

Infra-red Spectra.

The spectra of the solid compounds were measured by Dr. R.A. Jones or Dr. A.G. Moritz of the Department of Organic Chemistry, University of Adelaide, using a Grubb-Parsons DB1 Spectrophotometer, fitted with sodium chloride optics. The medium used for examination of the various compounds is indicated at the appropriate place in Chapter 7. The vapour phase spectrum was measured with a Perkin-Elmer Infracord, fitted with sodium chloride optics.

Vapour Phase Chromatography.

A Perkin-Elmer 154C Fractometer, fitted with a two metre column of silica gel was used. The measurements were made by Dr. T.N. Bell of the Department of Physical and Inorganic Chemistry, University of Adelaide.

Ultra-violet Spectra.

Ultra-violet spectra were measured with an Optica Model CF_4 double beam recording spectrophotometer. All compounds were investigated in ethanol solution. Benzene free ethanol was refluxed over and distilled from sodium hydroxide.

2. Reactants.

Trifluoroiodomethane was prepared by the reaction between iodine and silver trifluoroacetate,[4] and was purified by trap to trap distillation until a molecular weight of 196 ± 1 (Calc. for CF_3I: M = 196) was obtained. No impurity could be detected by vapour phase chromatography.

Triphenylphosphine and Triphenylarsine. Reagent grade samples of these compounds were recrystallized from ethanol until microanalytically pure.

Phenyldimethylamine. A reagent grade sample of this compound, dried by molecular sieves, was used.

Phenyldimethylphosphine was prepared by the reaction between phenyldichlorophosphine and methylmagnesium iodide,[5] and was purified by distillation at reduced pressure in a nitrogen atmosphere. Its identity was confirmed by conversion to the derivatives phenyltrimethylphosphonium iodide, recrystallized from ether/ethanol, m.p. 229-230° (lit.[6,7] 226-227°, 236°) (Found: C, 38.7; H, 5.2; I, 45.3. Calc.

for $C_9H_{14}IP$: C, 38.6; H, 5.0; I, 45.3%), and phenyldimethylethylphosphonium iodide, recrystallized from ether/ethanol, m.p. 146° (lit.[8] 137°) (Found: C, 41.0; H, 5.55; I, 43.1. Calc. for $C_{10}H_{16}IP$: C, 40.8; H, 5.4; I, 43.1%).

3. The Reaction of Triphenylphosphine with Trifluoroiodomethane.

The details of the amounts of reactants used in the various experiments are given in Table 7.1.

Experiments 2-6 (Table 7.1).

Triphenylphosphine was found to be soluble in liquid trifluoroiodomethane at room temperature, but no reaction occurred. On heating, the triphenylphosphine melt on the bottom of the reaction vessel was slowly converted to a yellow viscous oil. On removal of the volatiles a yellow glue was obtained. The volatiles from each experiment were fractionated through traps cooled to -95°, -131°, and -196°, and consisted primarily of unreacted trifluoroiodomethane, which condensed at -131°, and was identified by its molecular weight. In addition a small amount of volatiles (less than 5% of the total volatiles recovered by weight) was obtained in the trap cooled to -196°. This fraction had molecular weights in the range 100-165. Vapour phase chromatography of this fraction from experiment 4 showed that trifluoroiodomethane was present together with two more volatile components. The infra-red spectrum of the same sample enabled the presence of trifluoroiodomethane to be confirmed and indicated the presence of fluoroform. In particular a well resolved C-H stretching frequency at 3077 cm^{-1} was present. (The reported spectrum has a band at 3020 cm^{-1}.)[9] The third component may be hexafluoroethane, the bands of which[10] would be hidden by those of trifluoroiodomethane[11] and fluoroform.

The reactants from experiment 1 were recovered unchanged, while the residue obtained after removal of the volatiles in experiment 2 consisted primarily of unreacted triphenylphosphine. This substance was extracted from the residue with petroleum ether (b.p. 30-40°). In experiments 3-5 very little free triphenylphosphine could be extracted from the product by benzene. The qualitative tests and infra-red spectral measurements described in Chapter 7 were carried out with the products of experiments 3-6. In tests where the product was hydrolysed with aqueous base, potassium hydroxide (10-15% w/v) was used.

4. The Reaction of Triphenylarsine with Trifluoroiodomethane.

Triphenylarsine was soluble in trifluoroiodomethane at room temperature. Triphenylarsine (0.70 mmole) and trifluoroiodomethane (ca. 10 mmole) were found to react on heating for 28 hr. at 160° with the formation of a yellow-orange glue. The residue was soluble in ether from which a yellow solid was obtained on evaporation of the solvent. With petroleum ether (b.p. 30-40°) this gave triphenylarsine as the soluble fraction, and a small amount of yellow solid, which fumed and decomposed on exposure to the atmosphere, as the insoluble fraction.

5. The Reaction of Phenyldimethylamine with Trifluoroiodomethane.

The details of the amounts of the reactants used in a typical experiment are given in Table 7.3. After heating the reactants for ca. 20 hr. at ca. 180° a red colour had developed in the liquid layer.

Further heating resulted in the deposition of an orange-red solid, and, when heating was discontinued, virtually no liquid remained. After removal of the volatiles an orange-brown solid was obtained, which decomposed with swelling and melting in the range 120-200° (Found: C, 44.45; H, 5.4; I, 29.4; N, 5.75; F, 8.2%). Various properties of this substance are summarized in Chapter 7.

The volatiles were separated by trap to trap distillation (the method was the same as used to separate the volatiles from the reaction of triphenylphosphine with trifluoroiodomethane), and the components were characterized by their molecular weights. The composition of the volatiles is given in Table 7.3.

In another similar experiment phenyldimethylamine (7.9 mmole) was heated with trifluoroiodomethane (12.9 mmole) for 8 days at 175°, yielding fluoroform (2.5 mmole) and an orange-brown solid (Found: C, 45.5; H, 5.3; N, 5.4; I, 29.3%). The amount of fluorine present in this substance was not determined.

6. The Reaction of Phenyldimethylphosphine with Trifluoroiodomethane.

Phenyldimethylphosphine and trifluoroiodomethane do not react at room temperature, but reaction occurs readily at ca. 95°. After reaction the volatiles were removed and separated by trap to trap distillation, and the components were characterized by their molecular weights. The amounts of reactants used in the experiments and the constitution of the volatiles recovered are given in Table 7.5.

A cream-yellow semi-solid product was obtained in the reaction, which appeared to decompose when exposed to the air and could not be crystallized. The product from experiment 1 (Table 7.5) was dissolved in acetone and the resultant solution was saturated with mercuric iodide. This yielded yellow crystals, which, recrystallised from acetone/ethanol, had m.p. 158-159° (Found: C, 14.3; H, 1.9; Hg, 30.5; P, 4.1; I, 48.4; HgI_2 (by decomposition with excess triphenylphosphine in ethanol, using the method described in Chapter 5, section 5.3), 69.1. Calc. for $C_{16}H_{21}Hg_2I_5P_2$: C, 14.6; H, 1.6; Hg, 30.6; I, 48.4; HgI_2, 69.3%). If this compound is the mercuric iodide derivative of phenylmethylphosphinomethyldimethylphenylphosphonium iodide, the decomposition with triphenylphosphine must rupture a $P \longrightarrow HgI_2$ bond. This would be expected as the product of the reaction, $(Ph_3P)_2HgI_2$, has a very low solubility in ethanol, whereas the reactant complex, which may contain a $P \longrightarrow HgI_2$ bond, does dissolve appreciably. The quaternary iodide liberated in the decomposition reaction could not be crystallised.

In another similar experiment, phenyldimethylphosphine (7.0 mmole) and trifluoroiodomethane (*ca.* 20 mmole) were heated for 19 hr. at 100-105°. The product after removal of the volatiles was saturated with mercuric iodide in acetone. The solution yielded a yellow glue on attempted crystallisation after the addition of ethanol. This was refluxed with methyl iodide for 4 hr., from which yellow crystals were obtained, which, recrystallised from acetone/ethanol (twice), had m.p. 174-174.5° (Found: C, 14.0; H, 1.8; Hg, 26.8, 27.4; I, 51.7; F, 0; HgI_2 (by decomposition with excess triphenylphosphine), 62.6. Calc. for $C_{17}H_{24}Hg_2I_6P_2$: C, 14.0; H, 1.65; Hg, 27.6; I, 52.4; HgI_2, 62.6. Calc. for $C_9H_{14}HgI_3P$: C, 14.7; H, 1.9; Hg, 27.3; I, 51.9; HgI_2, 61.9%). After the decomposition reaction with triphenylphosphine, phenyltrimethylphosphonium iodide was recovered from the excess triphenylphosphine, and, recrystallised from ether/ethanol, had m.p. 226-229°

(with some decomposition) (Found: C, 38.75; H, 5.15%). The identification of the product was confirmed by its infra-red spectrum, which was identical to that of an authentic sample of phenyltrimethylphosphonium iodide.

The infra-red spectra and ultra-violet spectra of the mercuric iodide complexes obtained from the product of the reaction between phenyldimethylphosphine and trifluoroiodomethane are discussed in Chapter 7.

7. Solubilities in Liquid Trifluoroiodomethane.

Low temperature solubilities were obtained by condensing trifluoroiodomethane on a sample of the solute at liquid air temperatures, then warming the solute/solvent system to the required temperature by placing the reaction vessel in a suitable slush bath. For room temperature (ca. 20°) determinations the solute and trifluoroiodomethane were sealed in a Carius tube (40-60 ml. capacity). Where the solute was sparingly soluble or insoluble the conclusions were confirmed by allowing part of the liquid phase to pass over a warmed part of the vessel to see if solute traces remained after evaporation of the trifluoroiodomethane.

The system tetramethylphosphonium iodide/trifluoroiodomethane.

Tetramethylphosphonium iodide (0.22 g.) and trifluoroiodomethane (ca. 7 g.) were sealed together and allowed to warm to room temperature. A two layer system was obtained, the upper layer being colourless and the lower pale yellow. When the system was cooled to ca. -3°, the layers became miscible, and, on cooling to -40°, some crystallization of tetramethylphosphonium iodide occurred. The compounds were heated at 150° for 17 hr. On cooling the 2 phase 1 phase change was again observed at -3°. The volatiles were removed and fractionated, and consisted primarily of unchanged trifluoroiodomethane, with a trace of a more volatile compound, possibly hexafluoroethane, also present. Tetramethylphosphonium iodide was recovered essentially unchanged, though the aqueous solution of this compound contained a trace of "free" iodine.

The system tetramethylammonium iodide/trifluoroiodomethane.

Tetramethylammonium iodide (0.25 g.) was sealed with trifluoroiodomethane (ca. 8 g.). The iodide did not appear to dissolve. After heating at 150° for 12 hr., the reactants were recovered essentially unchanged. A possible trace of hexafluoroethane was also obtained, while the tetramethylammonium iodide had a faint brown colour, which may be due to a trace of iodine.

The system ferrocene/trifluoroiodomethane.

Ferrocene (0.13 g.) was sealed with trifluoroiodomethane (ca. 4 g.). Complete solution of the ferrocene occurred below room temperature, but no reaction was evident. After heating for 110 hr. at 130°, the reactants were recovered unchanged.

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APPENDIX

Details of Papers Published or Accepted for Publication.

Published

Deacon and West, "Iodomercurate Complexes with Group V Quaternary Iodides. Part I. Aqueous Decompositions and Absorption Spectra". J. Chem. Soc., 1961, 3929. Reprint appended.

Accepted for Publication

1. Deacon and West, "Iodomercurate Complexes with Group V Quaternary Iodides. Part II. Reactions with Triphenylphosphine". J. Chem. Soc., 1961, 5127. ~~in the press.~~ Photostat of the proofs appended.
2. Deacon and West, "The Reactions of Metal Complexes with Alkyl Halides. Part I. Reactions of Halo(triphenylphosphine)mercury(II) and Quaternary Halomercurate(II) Complexes". J. Inorg. Nuclear Chem., in the press. Proofs not yet available.

Deacon, G., & West, B. (1961). Iodomercurate complexes with Group V quaternary iodides. Part II. Reactions with triphenylphosphine. *Journal of the Chemical Society (Resumed)*, 5127-5131.

Deacon, G., & West, B. (1961). Iodomercurate complexes with group V quaternary iodides. Part I. Aqueous decompositions and absorption spectra. *Journal of the Chemical Society (Resumed)*, 3929-3935.