767. *Iodomercurate Complexes with Group V Quaternary Iodides. Part I. Aqueous Decompositions and Absorption Spectra.*

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Iodomercurate complexes containing the cations (M) NMe_4^+, PyH^+, PMe_4^+, Ph_3MeAs^+, and having the empirical formulæ $M_2[HgI_4]$, $M[HgI_3]$, $M_2[Hg_3I_8]$, or $M[Hg_2I_5]$ have been prepared. The nature of their decomposition in aqueous suspension has been established. The ultraviolet spectrum of a representative of each class of the iodomercurates has been determined.

Examples are known of four classes of quaternary iodomercurate complexes, involving univalent cations (M), *viz.*, (I) tetraiodomercurates $M_2[HgI_4]$, (II) tri-iodomercurates $M[HgI_3]$, (III) pentaiododimercurates $M[Hg_2I_5]$, and (IV) octaiodotrimercurates $M_2[Hg_3I_8]$. It has now been established that the tetramethylammonium and tetramethylphosphonium cations form complexes of classes (I)—(III), the triphenylmethylarsonium cation forms complexes of classes (I) and (II), and the pyridinium cation forms complexes of classes (I), (II), and (IV). Two previously reported compounds, *viz.*, bis(tetramethylammonium) octaiodotrimercurate(II)[1] and pyridinium pentaiododimercurate(II)[2] could not be authenticated. A solid with the composition of the former complex was found to yield the corresponding tri-iodomercurate and pentaiododimercurate on fractional recrystallisation, while attempts to prepare the latter complex gave dipyridinium octaiodotrimercurate(II). Factors affecting the isolation of quaternary tetrahalogeno-transition-metal complexes have been discussed.[3]

The compounds $[PyH]_2[HgI_4]$, $[PMe_4][HgI_3]$, $[NMe_4][Hg_2I_5]$, and $[PyH]_2[Hg_3I_8]$, are diamagnetic as is expected for a d^{10} structure of the mercuric ion.

Aqueous Decompositions.—Various water-insoluble quaternary iodomercurate complexes deepen in colour when washed with water,[1] and pyridinium iodomercurates undergo partial decomposition to mercuric iodide when similarly treated.[2] Bis(triethylsulphonium) tetraiodomercurate(II) lost diethyl sulphide and ethyl iodide and formed the tri-iodomercurate when heated with water.[4] It has now been established that a series of insoluble quaternary iodomercurates will decompose in water to form other insoluble iodomercurates, or mercuric iodide and a soluble quaternary iodide. The reactions follow a stepwise pattern thus:

$$\text{(i)}\quad M_2[HgI_4] \longrightarrow M[HgI_3] + M^+ + I^-$$

$$\text{(ii)}\quad 2M[HgI_3] \longrightarrow M[Hg_2I_5] + M^+ + I^-$$

$$\text{or}\qquad \text{(iii)}\quad 3M[HgI_3] \longrightarrow M_2[Hg_3I_8] + M^+ + I^-$$

$$\text{(iv)}\quad M[Hg_2I_5] \longrightarrow 2HgI_2 + M^+ + I^-$$

$$\text{(v)}\quad M_2[Hg_3I_8] \longrightarrow 3HgI_2 + 2M^+ + 2I^-$$

where (i) $M = NMe_4$, PMe_4, PyH, Ph_3MeAs; (ii) $M = NMe_4$, PMe_4; (iii), (v) $M = PyH$; and (iv) $M = PMe_4$. Triphenylmethylarsonium tri-iodomercurate(II) does not decompose further on boiling with water, which is consistent with the failure to prepare either a penta- or an octa-iodo-derivative for this cation. The course of the reaction of pyridinium tri-iodomercurate(II) is in agreement with the preparation of an octaiodo- and not a pentaiodo-derivative for this cation. The quaternary iodide eliminated in a particular step inhibits the next step, enabling an easy identification of the product to be made at each stage. Attempted decomposition of tetramethylphosphonium tri-iodomercurate(II) in the presence of a large excess of iodide resulted in the formation of the tetraiodomercurate.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of mercuric iodide

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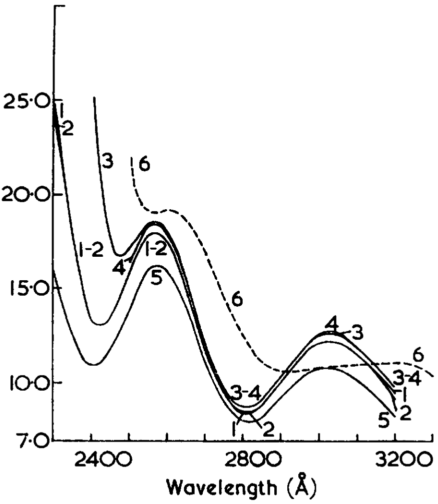
[1] Lal Datta, *J. Amer. Chem. Soc.*, 1913, **35**, 949.
[2] François, *Compt. rend.*, 1905, **140**, 861.
[3] Gill and Nyholm, *J.*, 1959, 3997.
[4] Balfe, Kenyon, and Phillips, *J.*, 1930, 2554.

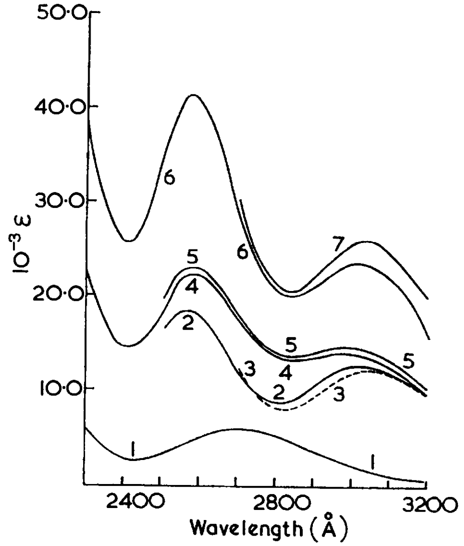
and a series of quaternary iodomercurates are shown in Figs. 1 and 2. Mercuric iodide has a single maximum in the region 2300—3200 Å in both methanol (Fig. 2, curve 1) and ethanol.[5] The spectra of tetramethylphosphonium tri-iodomercurate(II) alone, and in the presence of an equivalent molarity of iodide, and of bis(tetramethylphosphonium) tetra-iodomercurate(II) alone, and in the presence of a moderate excess of iodide * are similar, and have maxima at the same wavelengths in methanol (Fig. 1, curves 5, 2, 1, 3), suggesting that the tri-iodomercurate ion is the predominant iodomercurate species in each solution. The differences in absorption between the solutions are then due to the existence of the equilibrium $HgI_2 + I^- \rightleftharpoons HgI_3^-$, tri-iodomercurate-ion formation increasing with increased iodide concentration. The tetraiodomercurate ion is not present in a detectable amount, since it requires the addition of a large excess of iodide to a solution of the tetra-iodomercurate complex to produce a significant change in its spectrum (Fig. 1, curve 6). A theoretical spectrum for the undissociated tri-iodomercurate ion in methanol has been calculated for the region 2500—3200 Å (Fig. 1, curve 4), by a method of continuous approximations, and corresponds closely to the spectrum of bis(tetramethylphosphonium) tetra-iodomercurate(II) in the presence of a moderate excess of iodide (Fig. 1, curve 3). The calculations were based on the assumption that the absorption of the methanol solutions of tetramethylphosphonium tri- and tetra-iodomercurates in the region 2500—3200 Å was due to mercuric iodide and the tri-iodomercurate ion alone. Iodide absorption is sufficiently small to be neglected in this region (Table 2). Details of the calculations are given in the experimental section, and the data used in Table 2. An average value of the

FIG. 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. 2. *Absorption spectra in methanol and ethanol.*



1 HgI_2, 10·9 × 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 × 10^{-4}M in methanol.
5 $[PMe_4][Hg_2I_5]$, calc. for methanol.
6 $[PyH]_2[Hg_3I_8]$, 1·37 × 10^{-4}M in ethanol.
7 $[PyH]_2[Hg_3I_8]$, calc. for ethanol.

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* Below 2500 Å, the spectrum of this solution is different owing to iodide absorption. Tetramethylphosphonium iodide in ethanol has ε (2400 Å) *ca.* 10^3, the absorption increasing markedly at lower wavelengths. For other values of ε_{PMe_4I} see Table 2.

[5] Fromherz and Lih, *Z. phys. Chem.*, 1933, **167**, 103.

equilibrium constant for the reaction $HgI_2 + I^- \longrightarrow HgI_3^-$ in methanol at 25° also obtained, is $7{\cdot}5 \times 10^4$. Values have been reported for this constant in acetonitrile,[6] 9×10^5, and in water,[7] $6{\cdot}1 \times 10^3$.

The relationship between the spectra of tetramethylphosphonium tri- and tetra-iodomercurates is the same in ethanol as in methanol. The maxima are shifted to slightly longer wavelengths in ethanol, but the absorptions at the maxima are very similar in either solvent. The spectra of the pyridinium tri- and tetra-iodomercurates are similar to those of the corresponding tetramethylphosphonium salts in ethanol, but are complicated by pyridinium-ion absorption [8] at λ >2700 Å. (A summary of spectra in ethanol is given in Table 1.) A theoretical spectrum for the undissociated tri-iodomercurate ion in ethanol has been calculated for the region 2700—3200 Å. In ethanol, pyridinium and tetramethylphosphonium tri- and tetra-iodomercurates show a slight departure from Beer's law in the concentration range $0{\cdot}07$—$6{\cdot}5 \times 10^{-4}$M measured at the higher wavelength maximum where the absorption of the cations and iodide is negligible, the deviation being greater for the tri-iodomercurate complexes. The peaks become less distinct with dilution, but the positions of the maxima are unaltered. This behaviour is consistent with the presence

TABLE 1. *Ultraviolet absorption spectra of quaternary iodomercurates in ethanol.*

Compound	10^4M	$\lambda_{max.}$ (Å) ($10^{-3}\varepsilon$)	
$[PMe_4]_2[HgI_4]$	2·40	2580 (18·1)	3040—3060 (12·2)
$[PMe_4][HgI_3]$	3·08	2580—2590 (16·3)	3040—3060 (11·0)
$[PMe_4][Hg_2I_5]$	2·29	2590—2600 (22·6)	3000—3010 (14·3)
$[PyH]_2[HgI_4]$	2·82	2560—2570 (24·8)	3040—3050 (12·1)
$[PyH][HgI_3]$	4·15	2570 (19·7)	3030—3050 (11·0)

TABLE 2. *Initial data used in the calculation of "theoretical" extinction coefficients for undissociated* $[HgI_3]^-$.

	Optical densities (1 mm. cells)				
Å	D^a	D^b	D^c	D^d	$10^{-3}\,\varepsilon_{HgI_2}$
2500	0·557	0·480			3·2
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
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

Values of ε_{PMe_4I} in ethanol: 2500 Å *ca.* 10^2, 2600 Å *ca.* 30, 3200 Å *ca.* 10.

[a] $[PMe_4][HgI_3]$, $4{\cdot}02 \times 10^{-4}$M in methanol (25°). [b] $[PMe_4]_2[HgI_4]$, $3{\cdot}02 \times 10^{-4}$M in methanol (25°). [c] $[PyH][HgI_3]$, $4{\cdot}15 \times 10^{-4}$M in ethanol (*ca.* 20°). [d] $[PyH]_2[HgI_4]$, $2{\cdot}82 \times 10^{-4}$M in ethanol (*ca.* 20°). [e] $[HgI_2]$, $10{\cdot}9 \times 10^{-4}$M in methanol (*ca.* 20°). Values for ε_{HgI_2} in ethanol taken from data of Fromherz and Lih.[5]

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[6] Ellendt and Cruse, *Z. phys. Chem.* (*Leipzig*), 1952, **201**, 130.

[7] Sillén, *Acta Chem. Scand.*, 1949, **3**, 539.

[8] Hughes, Jellinek, and Phillips, *J. Phys. and Colloid Chem.*, 1949, **53**, 410.

of the tri-iodomercurate ion as the dominant iodomercurate species, in equilibrium with mercuric iodide and iodide ions.

The shift of the higher-wavelength maximum of bis(tetramethylphosphonium) tetraiodomercurate(II) towards the visible region in the presence of a large excess of iodide (Fig. 1, curve 6) is due to the presence of significant amounts of the tetraiodomercurate ion. The indistinct nature of the maximum shows that a considerable amount of the tri-iodomercurate ion is still present. The lower-wavelength maximum is masked by iodide absorption. The spectrum of mercuric iodide in aqueous and ethanolic solutions of alkali-metal iodides shows two absorption maxima, at 2670 and 3230 Å in water, and 2730 and 3290 Å in ethanol.[5] Distinct maxima were only obtained with very high ratios of MI : HgI_2, or by using much higher concentrations than in the present work (where MI : HgI_2 = *ca.* 2 : 1). The spectra were considered to show the presence of *one* iodomercurate species only, *viz.*, the tetraiodomercurate ion.

Since the spectrum of tetramethylphosphonium pentaiododimercurate(II) (Fig. 2, curve 4) is similar to those of the corresponding tri- and tetra-iodomercurate complexes in methanol, with only slight shifts in the positions of the absorption maxima, and with enhanced absorption compared with the theoretical curve for undissociated $[HgI_3]^-$ in the region 2500—3000 Å (Fig. 2, curve 2) where mercuric iodide has its absorption band (Fig. 2, curve 1), it is considered that in solution the pentaiododimercurate complex dissociates into mercuric iodide and tri-iodomercurate. A theoretical spectrum for tetramethylphosphonium pentaiododimercurate(II) (Fig. 2, curve 5) has been constructed by assuming complete dissociation into HgI_2 and $[HgI_3]^-$, and using the measured extinction coefficients of HgI_2 and those calculated for undissociated $[HgI_3]^-$ ions; it closely agrees with that determined experimentally for the pentaiodo-complex. The differences between the curves can be explained by some further dissociation, *viz.*, of $[HgI_3]^-$ into mercuric iodide and iodide. The value of the equilibrium constant indicates that one molar equivalent of mercuric iodide is insufficient to prevent dissociation of $[HgI_3]^-$ ions at the concentrations studied. In ethanol the complex shows good agreement with Beer's law at 3000 Å in the concentration range 0·09—3·00 × 10^{-4}M and the positions of the maxima are unaltered on dilution. This would not be expected if significant amounts of $[Hg_2I_5]^-$ ions were present at the higher concentrations studied.

Similarly the shape of the spectrum of pyridinium octaiodotrimercurate(II) can be explained as being due to the dissociation of the complex into mercuric iodide and tri-iodomercurate ions $[Hg_3I_8]^{2-} \longrightarrow 2[HgI_3]^- + HgI_2$. A theoretical curve for the complex has been constructed for the region 2700—3200 Å by assuming complete dissociation into these components. Greater absorption is shown by the theoretical curve throughout this region, which may be explained by dissociation of $[HgI_3]^-$ ions into mercuric iodide and iodide as in the case of the pentaiodo-compound. This dissociation is expected to be greater for the octaiodo-complex, as the initial ratio of $[HgI_3]^-$: HgI_2 is 2 : 1 (1 : 1 for the pentaiodo-complex) so that the effect of mercuric iodide in decreasing the dissociation of $[HgI_3]^-$ will be smaller in solutions of the octaiodo-derivative. The octaiodo-complex shows good agreement with Beer's law at 3020 Å in the concentration range 0·05—2·75 × 10^{-4}M and the absorption maxima are scarcely altered by dilution.

EXPERIMENTAL

Preparations.—Two general methods of preparation of quaternary iodomercurates were used.

Method 1. Stoicheiometric quantities of a quaternary iodide and mercuric iodide were heated in acetone. The products were obtained by evaporation of the solvent until crystallization began.

Method 2. The stoicheiometric quantity of mercuric iodide, dissolved in aqueous potassium iodide, was added to the correct amount of quaternary iodide dissolved in water. The desired iodomercurate was immediately precipitated. The method was satisfactory for preparing tri- and tetra-iodomercurates, the compound precipitated depending only on the ratio of quaternary iodide to mercuric iodide and being independent of the presence of excess of potassium iodide provided the reaction mixture was not heated.

All the compounds prepared were recrystallized from acetone, ethanol, or a mixture of both. The solubility of tetraiodomercurate complexes in acetone is much lower than that of the other complexes. The solubilities of the pyridinium compounds are generally higher in acetone or ethanol than the complexes of other cations studied.

Bis(tetramethylammonium) tetraiodomercurate(II). Method 1 gave fine cream needles (difficulty was experienced in using all the quaternary iodide), m. p. >300° (lit.[1] gives no value) (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 slender pale-yellow needles, m. p. 243° (lit.[9] m. p. >200°) (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 bright-yellow microcrystals on complete evaporation of the solvent; they had m. p. *ca.* 180—181° (lit.[1] gives no value). On fractional crystallization from acetone–ethanol the pentaiododimercurate was first obtained (m. p. and mixed m. p. 189°) followed by tetramethylammonium tri-iodomercurate(II) (m. p. and mixed m. p. 242·5—244°).

Dipyridinium tetraiodomercurate(II). François's method [2] gave material, m. p. *ca.* 168° (lit.[2] m. p. 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 stoicheiometric quantities of pyridinium tetraiodomercurate(II) and mercuric iodide were dissolved in acetone; the compound crystallized as yellow microcrystals after the addition of ethanol and had m. p. 149·5° (lit.[2,10] m. p. 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%).

Dipyridinium octaiodotrimercurate(II). The stoicheiometric quantities of the tetraiodomercurate and mercuric iodide required to form the pentaiododimercurate were heated in acetone. Mercuric iodide failed to dissolve completely. The resulting solution yielded the octaiodotrimercurate as yellow microcrystals, m. p. 101·5—102·5° (lit.[2] 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%). Use of the correct proportions of tri-iodomercurate and mercuric iodide for the pentaiododimercurate in acetone also gave the octaiodo-derivative. A solid, m. p. *ca.* 130° (reported value [2] of m. p. for $[PyH][Hg_2I_5]$ is 121°), containing more mercuric iodide than that required for the octaiodo-complex could be obtained from ethanol. On addition of acetone, in an attempt to recrystallize it, 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%).

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 two products was shown by mixed m. p. 197·5° and identical *X*-ray powder photographs.

Tetramethylphosphonium pentaiododimercurate(II). Method 1 gave deep-yellow needles, m. p. 172° (lit.[11] m. p. 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, m. p. 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

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[9] Barker and Porter, *J.*, 1920, **117**, 1303.

[10] McCleland and Wilson, *J.*, 1932, 1263.

[11] Partheil and van Haaren, *Arch. Pharm.*, 1900, **238**, 41; Haszeldine and West, *J.*, 1956, 3631.

method 1 and gave a glue-like product. Extraction with cold acetone gave mercuric iodide and the tri-iodo-derivative (m. p. and mixed m. p. 140°).

Aqueous Decompositions.—(a) *Tetraiodomercurate complexes.* A sample of a complex was suspended in water and warmed (*ca.* 60°) until the cream colour of the solid had changed to the pale yellow of the tri-iodomercurate. The product was recrystallized from acetone–ethanol. *X*-Ray powder photographs were used to confirm the identity of the product.

(i) Bis(tetramethylammonium) tetraiodomercurate(II) (0·183 g.) was heated with water (15 ml.) for 10 min., giving the tri-iodomercurate complex (0·141 g.; 98%), m. p. and mixed m. p. 244·5°. Iodide was detected in the filtrate.

(ii) Dipyridinium tetraiodomercurate(II) (0·552 g.) was heated with water (25 ml.) for 15 min., giving the tri-iodomercurate complex (0·385 g.), m. p. and mixed m. p. 149—150°. Evaporation of the filtrate to crystallization gave more tri-iodomercurate (0·064 g.; 78%), m. p. 150°, mixed m. p. 149—150°.

(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%), m. p. and mixed m. p. 197·5°. Iodide was detected in the filtrate. In a similar experiment a suspension of tetraiodomercurate complex was boiled in water until the colour of the solid had changed to bright yellow. The product was impure tetramethylphosphonium pentaiododimercurate(II).

(iv) Bis(triphenylmethylarsonium) tetraiodomercurate(II) (0·191 g.) was boiled with water (20 ml.) for 20 min. giving the tri-iodomercurate (0·05 g.; 35%), m. p. 140°, mixed m. p. 139·5—140°. The low yield was presumably due to dissolution of some product in the aqueous iodide solution.

(b) *Tri-iodomercurate complexes.* The method was similar to that used for tetraiodomercurate decompositions. The pale yellow complex was warmed until a bright yellow complex had formed. *X*-Ray powder photographs were used to confirm the identity of the product.

(i) Tetramethylammonium tri-iodomercurate(II) (0·240 g.) was heated (*ca.* 80°) with water (30 ml.) for 10 min., yielding the pentaiododimercurate complex (0·193 g.; 95%), 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.) (*ca.* 80°) until a melt began to form on the bottom of the vessel (15 min.). Pyridine was evolved during the reaction. On cooling, the melt solidified and some crystals were deposited from the solution. This crystalline material 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.) consisted mainly of the octaiodotrimercurate complex, together with some mercuric iodide. The total yield was 75%.

(iii) Tetramethylphosphonium tri-iodomercurate(II) (0·410 g.) was shaken with water (40 ml.) at room temperature for 1 hr.; the colour of the solid deepened. The suspension was then heated to *ca.* 80° and immediately cooled, giving impure pentaiododimercurate (0·365 g.; 68%). Complete degradation would provide 0·344 g. of product. The filtrate was quantitatively analysed for iodide and corresponded to 69% reaction. The solid was further degraded by boiling it with water for 5 min., and gave tetramethylphosphonium pentaiododimercurate(II), m. p. and mixed m. p. 172°. The reaction could, however, be completed in one step. The tri-iodomercurate (0·122 g.) was degraded by heating it with boiling water for 5 min., yielding pentaiododimercurate (0·096 g.; 94%), m. p. 172—173°, mixed m. p. 171°.

Attempted degradation of the tri-iodomercurate in the presence 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.) to *ca.* 80°; the suspended tri-iodomercurate then dissolved. On cooling, tetramethylphosphonium tetraiodomercurate(II) was obtained (0·058 g.; 38%), m. p. >300°.

(c) *Other degradations attempted.* (i) Triphenylmethylarsonium tri-iodomercurate(II) was unchanged after being heated with water at 80—100° for 35 min., and vigorously boiled for another 5 min.; it had m. p. and mixed m. p. 138·5—139°. This treatment was considerably more severe than that required to bring about decomposition of other tri-iodomercurates.

(ii) Tetramethylphosphonium pentaiododimercurate(II) and pyridinium octaiodotrimercurate(II) slowly decomposed to mercuric iodide when boiled with water, pyridine being detected by smell from the latter.

Ultraviolet Absorption Spectra.—These were determined with a Unicam S.P. 500 spectrophotometer, standard silica cells being used. A constant-temperature cell housing (S.P. 570) was employed for determinations at 25° (Fig. 1, curves 1—3, 5; Fig. 2, curve 4). Other determinations were at room temperature (*ca.* 20°).

Solvents were reagent grade, refluxed over, and distilled from, sodium hydroxide.

Calculation of the Theoretical Spectra and Equilibrium Constants.—If the absorption of methanol solutions of tetramethylphosphonium tri- and tetra-iodomercurates in the region 2500—3200 Å is due to the tri-iodomercurate ion and mercuric iodide, the optical density of either solution is given by the equation

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

where $c_{HgI_3^-}$, c_{HgI_2} are equilibrium concentrations. By initially assuming a value of $\varepsilon_{HgI_3^-}$ at a particular wavelength, and using the experimental optical densities for solutions of the tri- and tetra-iodomercurate complexes and the independently obtained value of ε_{HgI_2} for the same wavelength, the equilibrium composition of the solutions, the equilibrium constant for the reaction $HgI_2 + I^- \rightleftharpoons HgI_3^-$ in methanol at 25°, and $\varepsilon_{HgI_3^-}$ were obtained by a converging series of continuous approximations. The process was repeated at other wavelengths. The calculated values of the equilibrium constant are very sensitive to small errors in the measured optical densities, whereas the calculated extinction coefficients are not. This accounts for the variation in 16 values of the equilibrium constant, from $6{\cdot}1$ to $8{\cdot}5 \times 10^4$. The theoretical spectrum of the tri-iodomercurate ion in ethanol was similarly calculated by using the observed spectra of pyridinium tri- and tetra-iodomercurates and the reported spectrum for mercuric iodide in ethanol.[5] Solutions were not maintained at a constant temperature for the measurement of these spectra, hence the equilibrium constants varied considerably. The values however were of the same order, *viz.* 10^5, as those obtained in methanol. No account has been taken of ion-pair formation.

Magnetic Measurements.—These were carried out by Gouy's method.

Microanalyses.—These were carried out by the Commonwealth Scientific and Industrial Research Organization analytical laboratories (Melbourne).

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