CCCXXXIX.—*The Parachor and Chemical Constitution. Part XV. The Constitution of Sulphonium and Ammonium Mercuri-iodides (Iodomercuriates).*

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THE sulphonium mercuri-iodides of the general formula R_3SHgI_3 are of interest in connexion with the electronic theory of valency since they have been formulated with six groups attached to a central sulphur atom (Hilditch and Smiles, J., 1907, **91**, 1398). These substances can be prepared either by the interaction of an alkyl sulphide with an alkyl iodide in the presence of mercuric iodide, or by the combination of a sulphonium iodide with mercuric iodide. Pope and Neville (J., 1902, **81**, 1097, 1552) found that an optically active sulphonium salt gave an inactive mercuritri-iodide, whereas (Pope and Harvey, J., 1901, **79**, 840) an optically active ammonium salt gave an active mercuritri-iodide of the general formula R_4NHgI_3. We have therefore made a comparative study of the properties of some sulphonium and ammonium mercuritri-iodides in the hope of finding some explanation of this difference in behaviour.

For this investigation we have chosen fusible substances so that their parachors could be determined. In the sulphonium series the dibenzyl-methyl- and -ethyl-sulphonium mercuritri-iodides described by Hilditch and Smiles (*loc. cit.*) fulfil this condition, and to these we have added the n-*propyl* and n-*butyl* derivatives which have not been previously described.

In the ammonium series we have examined the phenyl-trimethyl, -dimethylethyl, -methyldiethyl, and -triethyl compounds described by Barker and Porter (J., 1920, **117**, 1308). These substances are all readily soluble in acetone and acetonitrile, sparingly soluble in alcohol, and insoluble in benzene and ligroin. This suggested that they were polar in character, and measurement of the conductivity of acetone solutions showed that they were all strong binary electrolytes.

Table I gives the conductivities found for the sulphonium compounds in acetone at 26°, the dilution v being given in litres; these are of the same order of magnitude as the conductivities of typical binary electrolytes in this solvent, *e.g.*, $N(C_3H_7)_4I$ gives $\lambda_{25^\circ} = 112{\cdot}6$ at $M/100$ (Walden, Ulich, and Birr, *Z. physikal. Chem.*, 1927, **131**, 34). Furthermore, the change of conductivity with dilution is in good agreement with the equation developed by Onsager (*Physikal. Z.*, 1926, **27**, 228; 1927, **28**, 277) for a completely dissociated uni-univalent electrolyte. This equation may be written

$$\lambda = \lambda_\infty - \left(\frac{5{\cdot}78 \times 10^5}{(DT)^{3/2}}\lambda_\infty + \frac{58}{(DT)^{1/2}\eta}\right)\sqrt{2c} \quad . \quad . \quad (1)$$

where D is the dielectric constant of the solvent and η its viscosity. For acetone at 25°, $D = 21{\cdot}5$ (Walden, *Z. physikal. Chem.*, 1909, **70**, 569); Hilditch and Dunstan (*Z. Elektrochem.*, 1912, **18**, 185) give $\eta_{25^\circ} = 0{\cdot}00305$, whilst interpolation in the data of Thorpe and Roger (*Phil. Trans.*, 1894, **185**, 397) gives $\eta_{26^\circ} = 0{\cdot}00315$. If we adopt the mean, $\eta_{26^\circ} = 0{\cdot}0031$, equation (1) becomes

$$\lambda = \lambda_\infty - (1{\cdot}586\,\lambda_\infty + 330)\sqrt{c} \text{ or } \lambda_\infty = (\lambda + 330\sqrt{c})/(1 - 1{\cdot}586\sqrt{c}).$$

TABLE I.

Conductivity of dibenzylalkylsulphonium mercuritri-iodides in acetone at 26°.

		$\lambda_{obs.}$				λ_∞.			
v.	$\sqrt{c}$.	Me.	Et.	Pr.	Bu.	Me.	Et.	Pr.	Bu.
2500	0·0200	154	—	153	—	166	—	165	—
1600	0·0250	—	—	—	148	—	—	—	163
1200	0·0289	—	145	—	—	—	162	—	—
1000	0·0316	143	—	145	—	162	—	164	—
800	0·0353	—	145	—	141	—	166	—	162
600	0·0408	—	139	—	—	—	163	—	—
500	0·0447	140	—	—	—	165	—	—	—
400	0·0500	—	136	132	133	—	166	161	162
250	0·0632	127	—	—	—	164	—	—	—
200	0·0707	—	121	120	120	—	163	162	162
100	0·1000	113	109	112	108	174	169	172	168

The values of λ_∞ calculated by this formula are given on the right-hand side of Table I; it will be seen that they are nearly constant except for the most concentrated solutions. The agreement with Onsager's equation is shown graphically in Fig. 1, in which λ is plotted against $\sqrt{c}$. The straight line corresponds to the Onsager formula with $\lambda_\infty = 164$.

The corresponding data for the ammonium compounds are colected in Table II. Here again the conductivities indicate that the substances are binary electrolytes, although the agreement with the Onsager equation is not so good. The deviation from this equation is, however, in the opposite direction to that which would be expected for incomplete dissociation.

FIG. 1.

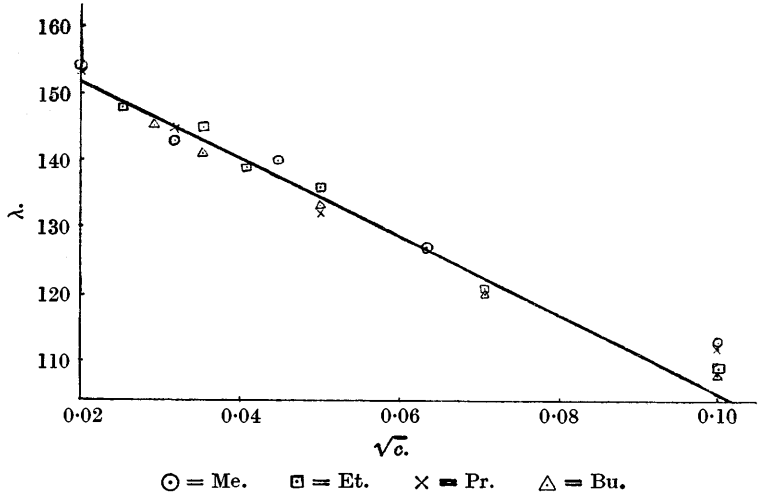


TABLE II.

Conductivities of phenyltrialkylammonium mercuritri-iodides in acetone at 26°.

		$\lambda_{obs.}$				λ_{∞}.			
v.	√c.	Me_3.	Me_2Et.	$MeEt_2$.	Et_3.	Me_3.	Me_2Et.	$MeEt_2$.	Et_3.
1600	0·0250	157	157	158	152	172	172	173	167
800	0·0353	152	153	153	148	173	174	174	169
400	0·0500	145	146	147	139	175	176	177	169
200	0·0707	137	137	137	127	180	180	180	169
100	0·1000	126	124	125	117	189	187	188	179
50	0·1414	116	116	114	106	210	210	208	197

It should be noted that the fourth substance, which is a dimercuripentaiodide (pentaiododimercuriate), $Et_3PhNHg_2I_5$, gives conductivities which indicate dissociation into two ions only.

Molecular weights were determined by the ebullioscopic method in acetone, a modified form of Cottrell's apparatus (*J. Amer. Chem. Soc.*, 1919, **41**, 721) being used. The results are given in Table III, the concentrations (c) being in g.-mols. per l. Owing to the small values of ΔT for substances of such high molecular weight, the accuracy is probably not greater than 8%. The values of the van 't Hoff factor ($i = M$, calc./M, obs.) again indicate dissociation into two ions; the dimercuripentaiodide appears to be rather more completely dissociated than the other substances.

TABLE III.

Molecular weights (ebullioscopic) in acetone.

	$MeBz_2SHgI_3$.			$EtBz_2SHgI_3$.		
c	0·0396	0·0816	0·1253	0·0467	0·0612	0·1070
M, obs.	541	569	572	549	590	580
i	1·50	1·42	1·42	1·50	1·38	1·40
	$PrBz_2SHgI_3$.			$BuBz_2SHgI_3$.		
c	0·0395	0·0783	0·1183	0·0536	0·1038	
M, obs.	594	587	588	612	609	
i	1·41	1·41	1·41	1·39	1·40	
	$Me_3PhNHgI_3$.			$Me_2EtPhNHgI_3$.		
c	0·0465	0·0930		0·0453	0·0906	
M, obs.	462	506		445	494	
i	1·55	1·42		1·64	1·48	
	$MeEt_2PhNHgI_3$.			$Et_3PhNHg_2I_5$.		
c	0·0406	0·0828		0·0284	0·0568	
M, obs.	451	487		539	593	
i	1·65	1·53		2·25	2·03	

The next question which arises is the nature of the two ions into which these substances are divided. In the ammonium series, since the nitrogen atom has its octet completed by sharing with four alkyl groups, it is highly improbable that it can also be attached to a mercury or an iodine atom. Hence the ammonium salts may be taken to have the structure $[R_4N]^+[HgI_3]^-$. The sulphur atom in the sulphonium compounds possesses an unshared pair of electrons which might link with the mercury atom, giving a complex of the type $[R_3SHgI_2]^+I^-$; on the other hand, the close similarity between the ammonium and sulphonium series is more compatible with the structure $[R_3S]^+[HgI_3]^-$.

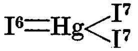
If the anion is an iodide ion, then its concentration should be capable of measurement by means of the cell

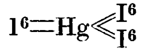
$$\mathrm{Ag}\;\Bigg|\;\begin{array}{c}M/100\text{-KI in}\\ \text{acetone,}\\ \text{saturated AgI}\end{array}\;\Bigg\|\;\begin{array}{c}M/100\text{-}R_3SHgI_3\\ \text{in acetone,}\\ \text{saturated AgI}\end{array}\;\Bigg|\;\mathrm{Ag}.$$

An attempt was made to set up this cell, but it was found that silver iodide was readily soluble in a solution of any of the sulphonium iodides. Hence, not only is the concentration of iodide negligibly small in these solutions, but this ion is removed probably to form the more stable ion $[HgI_4]^{--}$ which is known in aqueous solutions.

The cell $\mathrm{Hg}\;\Big|\begin{array}{c}M/100\text{-}HgCl_2\\ \text{in acetone}\end{array}\Big\|\begin{array}{c}M/100\text{-}Me_3SHgI_3\\ \text{in acetone}\end{array}\Big|\;\mathrm{Hg}$ was set up, and found to have an *E.M.F.* of 0·145 volt, with the electrode in contact with mercuric chloride positive. The small conductivity of mercuric chloride in acetone solution indicates a small degree of dissociation (much less than 10% at *M*/100), hence the amount of free mercuric ion in the solution of the sulphonium mercuri-iodide is less than 10^{-6} of the total mercury present [conc. = $10^{(3 + 0\cdot145/0\cdot029)}$ = 10^{-8}]. The $[HgI_3]^-$ ion seems, therefore, to be very stable.

Since both series of compounds appear to contain the HgI_3^- ion, the only remaining question is its electronic structure. Two formulæ are possible; in (I) the negative charge is associated with the iodine

(I.)

$I^6{=}Hg{<}^{I^7}_{I^7}$


$I^6{=}Hg{\ll}^{I^6}_{I^6}$
(II.)

atoms which are linked to the mercury atom by singlet linkages, whilst in (II) the mercury is negative and all the iodine atoms are held by duplets. These structures should be distinguishable by means of the parachor, since the singlet links in (I) correspond to a decrement of 24·8 units. Since, however, the substances are all electrolytes, the interpretation of the parachors may be obscured by the large anomalies already noted in fused salts (Sugden and Wilkins, J., 1929, 1291).

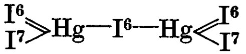
TABLE IV.

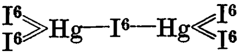
Parachors.

Substance.	[*P*] obs.	[*P*] calc. (I).	[*P*] calc. (II).
$Et(PhCH_2)_2SHgI_3$	915·2	916·9	941·7
$Pr(PhCH_2)_2SHgI_3$	952·0	955·9	980·7
$Bu(PhCH_2)_2SHgI_3$	1000·0	994·4	1019·2
$Me_3PhNHgI_3$	719·1	688·0	712·8
$Me_2EtPhNHgI_3$	754·0	727·0	751·8
$MeEt_2PhNHgI_3$	789·5	766·0	790·8
$Et_3PhNHg_2I_5$	1060·0	1031·2 (see III)	1056·0 (see IV)

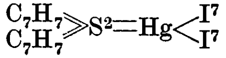
The experimental values of the parachors collected in Table IV are compared with the values calculated for formulæ (I) and (II). It will be seen that the sulphonium compounds give parachors in good agreement with the singlet formula (I), whilst the ammonium compounds are in better agreement with (II). It is, of course, highly improbable that there are two isomeric HgI_3^- ions; hence it must be supposed, either that (I) is the correct formula and that the ammonium salts exhibit a large salt error, or that (II) is correct and that the sulphonium salts show a negative salt error. Until more information has been obtained as to the types of salt which are likely to exhibit parachor anomalies, it is not possible to decide between these two hypotheses.

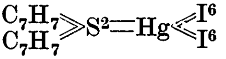
The formula of the dimercuripentaiodide can also be written in two ways, *viz.*, (III) and (IV), which contain 4 and 2 singlet linkages respectively. The values given for [*P*] calc. in the table correspond with these formulæ; it will be seen that the observed parachor is in good agreement with (IV).

(III.) 
$\begin{matrix}I^6\\I^7\end{matrix}\!>Hg-I^6-Hg<\!\begin{matrix}I^6\\I^7\end{matrix}$

 (IV.)
$\begin{matrix}I^6\\I^6\end{matrix}\!>Hg-I^6-Hg<\!\begin{matrix}I^6\\I^6\end{matrix}$

An additive compound of benzyl sulphide and mercuric iodide was also examined but was too unstable to permit of a parachor determination. It was found, however, that its solution in acetone has only a very small conductivity ($\kappa = 8{\cdot}4 \times 10^{-6}$ at $M/100$); hence it must be formulated as a non-polar molecule with the structure (V) or (VI).

(V.) 
$\begin{matrix}C_7H_7\\C_7H_7\end{matrix}\!>S^2=Hg<\!\begin{matrix}I^7\\I^7\end{matrix}$

 (VI.)
$\begin{matrix}C_7H_7\\C_7H_7\end{matrix}\!>S^2=Hg<\!\begin{matrix}I^6\\I^6\end{matrix}$

A preliminary account of the results of this investigation was given by one of us last year (Sugden, " The Parachor and Valency," Routledge and Sons, London, 1929, p. 153). Recently, Ray and Kumar (*J. Indian Chem. Soc.*, 1930, **7**, 297), having independently found that the conductivities of triethylsulphonium mercuri-iodide and phenacylmethylethylthetine mercuri-iodide in acetone are of the same order as those of binary electrolytes, have formulated these substances with the $[HgI_3]^-$ anion.

EXPERIMENTAL.

Parachors.—Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 158; 1924, **125**, 27), and densities by means of the U-shaped pyknometer described in J., 1924, **125**, 1171. The tables below are set out in the same manner as in earlier papers and need no further description.

Dibenzylethylsulphonium mercuritri-iodide, $C_{16}H_{19}SHgI_3$, $M =$ 824, prepared as described by Hilditch and Smiles (*loc. cit.*), had m. p. 116° (Found: Hg, 24·15. Calc.: Hg, 24·35%). Densities determined: $D_{4^\circ}^{120^\circ}$ 2·333, $D_{4^\circ}^{127^\circ}$ 2·302.

t	120°	122°	126°	
γ	45·33	44·20	42·95	
D	2·333	2·324	2·306	
Parachor	916·2	914·2	915·2	Mean 915·2

Dibenzyl-n-*propylsulphonium mercuritri-iodide*, $C_{17}H_{21}SHgI_3$, $M = 838$, was prepared in a similar manner, and recrystallised from acetone–alcohol; m. p. 78° (Found: Hg, 23·84. $C_{17}H_{21}SHgI_3$ requires Hg, 23·92%). Densities determined: $D_{4^\circ}^{77\cdot5^\circ}$ 2·312, $D_{4^\circ}^{85\cdot5^\circ}$ 2·296, $D_{4^\circ}^{94^\circ}$ 2·282, $D_{4^\circ}^{99\cdot5^\circ}$ 2·273, whence $D_{4^\circ}^{t^\circ} = 2{\cdot}446 - 0{\cdot}00174t$.

t	85·5°	91·5°	95·5°	
γ	45·96	45·53	45·10	
D	2·295	2·290	2·280	
Parachor	951·3	951·5	953·3	Mean 952·0

*Dibenzyl-*n*-butylsulphonium mercuritri-iodide*, $C_{18}H_{23}SHgI_3$, $M = 852$, was prepared in a similar manner; the condensation of the alkyl iodide with mercuric iodide and dibenzyl sulphide was very slow and required several days. After repeated crystallisation from acetone–alcohol, the substance melted at 81° (Found: I, 44·63. $C_{18}H_{23}SHgI_3$ requires I, 44·67%). Densities determined: $D_{4°}^{81·5°}$ 2·216, $D_{4°}^{91·5°}$ 2·202, $D_{4°}^{101·5°}$ 2·186, $D_{4°}^{112°}$ 2·173, whence $D_{4°}^{t°} = 2·335 - 0·00147t$.

t	85·5°	93·5°	100·5°	111°	
γ	45·62	44·30	42·98	42·20	
D	2·208	2·198	2·188	2·172	
Parachor	1003	1000	997	1000	Mean 1000

Phenyltrimethylammonium mercuritri-iodide, $C_9H_{14}NHgI_3$, $M = 717$. This and the following ammonium compounds were prepared by warming together in acetone solution equimolecular quantities of an alkyl iodide, a dialkylaniline, and mercuric iodide (compare Barker and Porter, *loc. cit.*). After crystallisation from acetone the substance melted at 137—138° (Found: I, 52·68. Calc.: I, 53·08%). Densities determined: $D_{4°}^{139°}$ 2·721, $D_{4°}^{146·5°}$ 2·710, $D_{4°}^{155·5°}$ 2·698, $D_{4°}^{160·5°}$ 2·689, whence $D_{4°}^{t°} = 2·923 - 0·00145t$.

t	147·5°	154°	157°	161·5°	
γ	54·61	53·68	53·48	53·06	
D	2·709	2·699	2·695	2·688	
Parachor	719·4	719·7	718·6	720·1	Mean 719·1

Phenyldimethylethylammonium mercuritri-iodide, $C_{10}H_{16}NHgI_3$, $M = 731$, melted at 97·5° (Found: I, 51·6. Calc.: I, 52·06%). Densities determined: $D_{4°}^{105°}$ 2·647, $D_{4°}^{113°}$ 2·636, $D_{4°}^{120°}$ 2·623, $D_{4°}^{129°}$ 2·612, whence $D_{4°}^{t°} = 2·810 - 0·00155t$.

t	109·5°	120°	128·5°	134·5°	
γ	55·24	53·21	52·42	51·93	
D	2·641	2·623	2·611	2·602	
Parachor	754·1	753·2	753·9	755·0	Mean 754·0

Phenylmethyldiethylammonium mercuritri-iodide, $C_{11}H_{18}NHgI_3$, $M = 745$, melted at 98·5°. Densities determined: $D_{4°}^{109·5°}$ 2·545, $D_{4°}^{116°}$ 2·537, $D_{4°}^{124°}$ 2·529, $D_{4°}^{130·9°}$ 2·520, whence $D_{4°}^{t°} = 2·669 - 0·00114t$.

t	107·5°	119°	126·5°	136°	
γ	52·41	51·72	51·20	50·52	
D	2·547	2·534	2·525	2·514	
Parachor	788·0	789·0	790·0	790·9	Mean 789·5

Phenyltriethylammonium dimercuripentaiodide, $C_{12}H_{20}NHg_2I_5$, $M = 1214$, was the chief product when diethylaniline was condensed with ethyl iodide and mercuric iodide, and required several crystallisations from acetone and alcohol for complete purification; m. p. 113° (Found: Hg, 32·97; I, 52·21. Calc.: Hg, 33·05; I, 52·28%). Barker and Porter (*loc. cit.*) describe $C_{12}H_{20}NHgI_3$ and $(C_{12}H_{20}N)_2HgI_4$. These substances were probably present in our mother-liquors, but we did not isolate them. Densities determined : $D_{4°}^{130·5°}$ 3·087, $D_{4°}^{136°}$ 3·077, $D_{4°}^{141·5°}$ 3·069, $D_{4°}^{147°}$ 3·059, whence $D_{4°}^{t°} = 3·300 - 0·00164t$.

t	124°	129·5°	134·5°	140·5°	
γ	53·38	52·90	52·42	51·88	
D	3·097	3·088	3·080	3·070	
Parachor	1059	1060	1060	1061	Mean 1060

Conductivities.—The acetone used as solvent was purified by drying over anhydrous sodium sulphate, followed by fractional distillation; the specific conductivity of the first batch (used for the sulphonium compounds) was $3·0 \times 10^{-6}$, whilst the second batch (used for the ammonium compounds) was more carefully fractionated and had a specific conductivity of $6·6 \times 10^{-7}$.

The conductivities were measured with a Gambrell Post Office Box accurate to 1 part in 1000 parts, alternating current of a frequency of 900 supplied by a valve oscillator being used. The cell constant was determined in the usual manner by measurements on aqueous solutions of potassium chloride. The accuracy of the molecular conductivities recorded in the theoretical part of this paper is estimated to be about 1%.

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