XLIII.—*Studies of Valency. Part VIII. Extinction Coefficients and Molecular Conductivities of Vernon's Isomeric α- and β-Dimethyltelluronium Salts. The Molecular Structure of Quadrivalent Tellurium Compounds.*

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Few substances possess a greater interest from the stereochemical point of view than the isomeric tellurium compounds prepared by Vernon in 1920 (J., 1920, **117**, 86, 889; 1921, **119**, 105, 687). The initial product, α-dimethyltelluronium di-iodide, $TeMe_2I_2$, prepared by the direct action of methyl iodide on tellurium (Demarçay, *Bull. Soc. chim.*, 1883, **40**, 99) is a dark-red solid, the salt-like character of which was demonstrated by Vernon, who converted it by the action of silver oxide into an "α-base," to which he assigned the formula $TeMe_2(OH)_2$. When the solution was evaporated to dryness, this α-base was converted into an anhydrous "β-base," $TeMe_2O$, which gave a series of isomeric β-salts, such as the β-di-iodide, when acted on by acids. No process was discovered by which the β-base or its salts could be reconverted directly into the α-compounds, but both bases gave the same dimethyltelluride on reduction, and on reoxidation a mixture of both bases was produced, although only the α-dihalide was formed when the telluride combined with a halogen. These isomeric bases behaved differently towards silver nitrate, ferrous and ferric chlorides, platinic chloride and picric acid; moreover, whereas the α-di-iodide gave oxy-iodide when treated with potassium carbonate, the β-di-iodide gave rise to trimethyltelluronium iodide, $TeMe_3I$, as the result of a wandering of a methyl group, which may be compared with the pinacol–pinacolin transformation. Since, however, their general physical and chemical properties resembled one another somewhat closely, Vernon concluded that the two series of compounds were stereoisomerides; and, since the α-base was converted into the anhydride of the β-base by dehydration, he identified the α-salts as the *trans*- and the β-salts as the *cis*-form of a quadrivalent complex with a planar or square configuration.

With the possible exception of the β-base, these tellurium compounds do not possess any marked odour; but they have the objectionable property of liberating dimethyltelluride by a slow progressive reduction, the effects of which may persist for long periods after contact with the original materials. The conditions which Vernon endured from this cause were indeed so intolerable that no further work on these compounds was attempted after the publication of his last paper in 1921, and it is only the fact that Vernon's own specimens were still in existence that led us to undertake the much less odious task of measuring their absorption spectra and molecular conductivities, without attempting to make any new material. At a later stage, when we had used up most of Vernon's specimens, we were fortunate in being able to secure from Dr. Alexander Scott an additional 20 grams of the α-di-iodide, and from this material a complete series of new specimens of the α- and β-salts was prepared.

The identity and purity of Vernon's specimens, which had been enclosed in sealed tubes and labelled, were guaranteed by their colour and beautiful crystalline character, but were also checked by melting-point determinations, which agreed precisely with Vernon's values. Only the β-di-iodide, which showed signs of decomposition, was recrystallised before being used. The purity of these specimens was also checked by comparison with fresh preparations from Dr. Scott's di-iodide, the only point of contrast being that the brilliant scarlet colour of Vernon's crystals of the α-di-iodide was not equalled in any other specimen. The β-dichloride, which Vernon described as "tinged" (but of which there was no specimen in his collection), was obtained quite free from colour, although with a rather lower melting point.

Absorption Spectra.

The striking difference in colour of the α- and β-dihalides shows that the isomerism of the α- and β-compounds must include some factor which is not expressed completely by merely putting two halogen atoms and two alkyl radicals at adjacent or at opposite corners of a square. Vernon himself (J., 1920, **117**, 86) showed that the β-compounds are more absorptive than the α-compounds in the ultra-violet as well as in the visible region of the spectrum; but it is difficult to assign any definite value to his transmission limits, in view of the fact that he did not detect the selective absorption which is the most striking characteristic of four out of six of these absorption spectra. The extinction coefficients of all the relevant compounds in Vernon's collection were therefore measured, but excluding in the first instance the β-dichloride, of which no specimen had been preserved.

These compounds were examined in $M/100$ to $M/10{,}000$-solutions in absolute alcohol, by methods which have already been described (J., 1924, **125**, 1921). When, however, the measurements of molecular conductivity had revealed the extreme sensitiveness of the dihalides to hydrolysis, even in the cold, the precaution was taken of plotting a fresh series of curves for a complete set of new samples prepared from Dr. Scott's iodide, but using as solvent a sample of alcohol which had been purified by distillation in an all-glass apparatus from freshly burnt lime (three times) and from a mercury–aluminium couple (twice), and was shown by density determinations to contain less than 0·1% of water. Slightly higher values were then obtained for the molecular extinction coefficients of some of the solutions, but without change in the form or character of the curves. On the other hand, when an alcoholic solution of the α-di-iodide was diluted with four times its volume of water, the maximum at $\lambda = 3570$, $\log \varepsilon = 3{\cdot}7$, was reduced to a mere step-out at $\log \varepsilon = 2{\cdot}4$, the absorptive power of the solution being reduced about 20-fold and the highly selective character of the absorption being largely destroyed. It is therefore possible that Vernon's failure to detect any selective absorption may have been due in part to a hydrolysis, which we should not have suspected if we had not measured the conductivities as well as the absorption spectra of the salts.

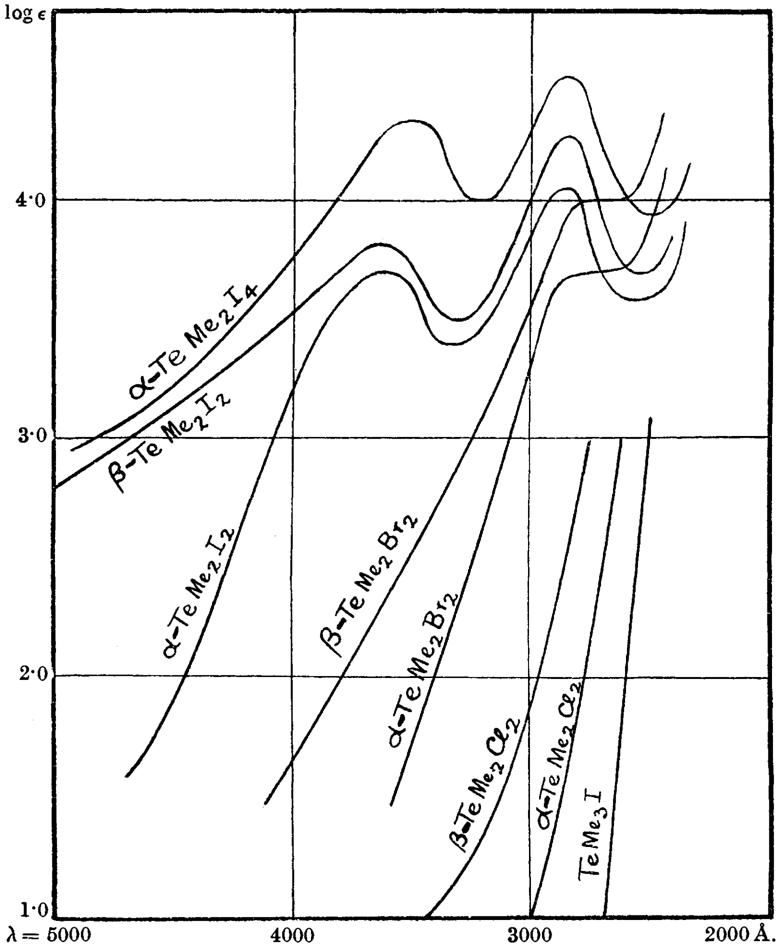
TABLE I.

Extinction Coefficients of Quadrivalent Tellurium Compounds.

	$\log \epsilon =$	1·0	2·0	3·0
$TeMe_3I$	$\lambda =$	2700	2600	2500
α-$TeMe_2Cl_2$	$\lambda =$	3000	2800	2600
β-$TeMe_2Cl_2$	$\lambda =$	3400	2900	2750
α-$TeMe_2Br_2$	Step out at $\lambda = 2800$ to 2600, $\log \epsilon = 3{\cdot}7$			
β-$TeMe_2Br_2$	,, ,, $\lambda = 2850$ to 2650, $\log \epsilon = 4{\cdot}0$			
α-$TeMe_2I_2$	Maxima at $\lambda = 3570$, $\log \epsilon = 3{\cdot}7$; $\lambda = 2840$, $\log \epsilon = 4{\cdot}05$			
β-$TeMe_2I_2$	,, $\lambda = 3660$, $\log \epsilon = 3{\cdot}8$; $\lambda = 2900$, $\log \epsilon = 4{\cdot}25$			
α-$TeMe_2I_4$	,, $\lambda = 3610$, $\log \epsilon = 4{\cdot}3$; $\lambda = 2900$, $\log \epsilon = 4{\cdot}5$			
KI_3	,, $\lambda = 3550$, $\log \epsilon = 3{\cdot}9$; $\lambda = 2900$, $\log \epsilon = 3{\cdot}95$			
CHI_3	,, $\lambda = 3450$, $\log \epsilon = 3{\cdot}4$; $\lambda = 2940$, $\log \epsilon = 3{\cdot}5$			

The new absorption curves are plotted in Fig. 1, and some of the more important extinction coefficients are set out in Table I. These observations show that, in spite of the marked differences in colour and in absorptive power to which reference has already been made, there is a fundamental similarity of *type* in the absorption spectra of the isomeric α- and β-compounds. For instance, the α- and β-dichlorides resemble trimethyltelluronium iodide in exhibiting only a general absorption of moderate intensity. The dibromides, however, both exhibit a well-marked "step-out," which is not shown by the dichlorides; thus, the molecular extinction coefficient of the α-dibromide remains almost constant at $\log \varepsilon = 3{\cdot}7$ over a range of 200 Å. from 2600 to 2800 Å. and, in the same way, the extinction coefficient of the β-compound remains almost constant at $\log \varepsilon = 4{\cdot}0$ over a similar range of wave-lengths. The most interesting compounds of the group are, however, the α- and β-di-iodides, both of which give the characteristic twin maxima which we have already recorded in the absorption spectra of iodoform and of potassium tri-iodide (J., 1926, 622). This result is in marked contrast with the behaviour of methylene di-iodide, CH_2I_2, which shows only a single maximum; it therefore gives additional force to Vernon's contention that " the relationship between the four tellurium valencies must be different from that generally assumed to exist between the carbon valencies in such a compound as methylene iodide."

FIG. 1.



Molecular extinction coefficients of quadrivalent tellurium compounds.

The α-tetraiodide, $TeMe_2I_4$, also gives two maxima, which agree fairly well in wave-length and intensity with those predicted for a mixture of one molecule of the α-di-iodide with one equivalent of the tri-iodide ion, the values for the latter being deduced from unpublished data for alcoholic solutions of the crystalline periodide, $C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{I_3}$. The tetraiodide can therefore be formulated in the usual way as the tri-iodide of a univalent kation, $[\overset{+}{Te}Me_2I]\overset{-}{I_3}$, in harmony with Vernon's conclusion that, since the α-di-iodide can be reproduced unchanged by removing a molecule of iodine from the tetraiodide, the latter compound does not contain sexavalent tellurium. It is noteworthy, however, that, whereas one atom of iodine in the α-di-iodide can be converted into a periodide, the second atom of iodine does not yield a tri-iodide radical, even when acted on by an excess of iodine, and that the β-di-iodide does not yield even a tetraiodide under similar conditions.

Molecular Conductivities.

The molecular conductivities of these compounds were determined in order to ascertain whether the dihalides behave as binary or as ternary electrolytes,* since it was expected that, if they were binary electrolytes, the limiting conductivities would be of the same order as in the case of tetramethylammonium chloride, which gives $\Lambda^{25°}_{\infty} = 46{\cdot}3 + 76{\cdot}55 = 122{\cdot}8$,† whereas if they were ternary electrolytes, the limiting conductivities might be nearly twice as great, since the hydrochloride of ethylenediamine,

$$\overset{-}{Cl}[\overset{+}{N}H_3{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}H_3]\overset{-}{Cl},$$

gives $\Lambda^{25°}_{\infty} = 80{\cdot}9 + 2 \times 76{\cdot}55 = 234{\cdot}0$.

For these conductivity measurements a calibrated wire-bridge was used. Most of the measurements were made with conductivity cells which had been used by Bousfield and Lowry (Fig. 8, *Phil. Trans.*, 1905, *A*, **204**, 298) when determining the conductivity of standard solutions of sodium hydroxide. Duplicate determinations in two different cells gave concordant results; but, since the dilutions were made by the ordinary volumetric and not by gravimetric methods, these results are not to be regarded as standard data. Only integral values have therefore been given for the molecular conductivities of the solutions. The conductivity water was prepared in a Bousfield still and had a specific conductivity of 1 to 2 gemmhos.

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* Compare Schilow's proof (*Z. anorg. Chem.*, 1924, **133**, 59) that mercurous nitrate is a ternary and not a binary electrolyte.

† There is very little difference between the three halogen ions, since Cl = 76·55, Br = 78·44, I = 77·2 at 25°.

The chief difficulty of the conductivity measurements arose from the sparing solubility of the salts in water. Vernon records that "on prolonged boiling" the α-di-iodide gives "an orange-red solution" which, on cooling, redeposits the iodide, leaving a perfectly colourless liquid, but that a "curious state of equilibrium" between the α-base and hydriodic acid results when a boiling saturated solution of the iodide is poured into a large excess of cold water. Under these conditions, a "fine yellow precipitate is formed" which quickly disappears, giving rise to a colourless solution, from which the iodide is at once precipitated on the addition of hydriodic acid. Vernon attributed these complex changes to hydrolysis of the iodide according to the equation $TeMe_2I_2 + 2H_2O \rightleftharpoons TeMe_2(OH)_2 + 2HI$; but the complexity of the phenomena suggested that this rather drastic treatment would not be likely to provide suitable conditions for a quantitative study of the conductivity of the undecomposed salts. We therefore chose, as a lesser evil, to dissolve the salts in the minimum amount of alcohol, and to drown the alcoholic solutions in cold conductivity-water, with the idea that the presence of a small proportion of alcohol would not alter the conductivities to such an extent as to prevent us from recognising the *type* of electrolyte with which we were dealing. Moreover, although the changes produced by heating the salts with water were obscure, there were sufficient data already available to show that the effect of alcohol on the *conductivity* of an aqueous electrolyte is about twice as great as its concentration; and in the same way, measurements of the vapour pressure of aqueous alcohol show that the effect of alcohol on the *activity* of the water is rather less than half as great as its concentration. The total effect produced by the presence of 2% of alcohol in the solution would therefore be to reduce the molecular conductivity of the salt by about 5%; moreover, since the proportion of alcohol was halved at each successive dilution, the conductivities of the weaker solutions would approximate more and more closely to those of solutions in pure water.

After most of Vernon's material had been used, a sufficient quantity of his α-di-iodide was left for an experiment on the "curious equilibrium" which is produced when the salt is hydrolysed by boiling water. A small quantity of the α-di-iodide was heated with water until it dissolved, and then poured into cold water; after the yellow precipitate had redissolved, the conductivity of the hydrolysed solution was measured. The values recorded agreed closely with those that had been obtained by diluting cold alcoholic solutions with a large excess of cold conductivity water, when the latter values were increased by 2½ times the percentage of alcohol which each solution contained. Thus, for the α-di-iodide, the following values were obtained:

v =	512 litres.	1024 litres.	2048 litres.	4096 litres.
Without alcohol $\Lambda^{25°}$ =	501(0)	509(0)	513(0)	517(0)
,, ,, ...	509(0)	511(0)	513(0)	515(0)
With alcohol (corr.)	506(4)	515(2)	517(1)	515(0·5)
,, ,, ,,	502(2·5)	510(1·25)	513(0·6)	516(0·3)
Mean	505	510	514	516

The percentage of alcohol in each solution is shown by the figures in brackets. The corresponding figures for the α-tetraiodide are: with alcohol (corr.) 482(4), 489(2), 494(1), 495(0·5).

These experiments showed that the hydrolysis of the di-iodide gives rise to the same final equilibrium, whether the solution is prepared by dilution with water from an alcoholic solution of the unhydrolysed salt, or by cooling a hot aqueous solution, in which hydrolysis may have proceeded far beyond the normal limits of hydrolysis at lower temperatures. This discovery opened the way for a new series of confirmatory experiments, as soon as additional material became available. Aqueous solutions of the α- and β-*bases* were therefore prepared from Dr. Scott's specimen of the di-iodide, by the methods described by Vernon. A complete series of six *normal* salts was then made by adding the halogen acids to the bases, and recrystallising the precipitated salt from alcohol. Finally, aqueous solutions of the six corresponding *hydroxy*-salts were prepared by mixing an aqueous solution of the α- or β-base with an equivalent quantity of the normal salt. The conductivities were then measured, *without the use of any alcohol*, by the methods described above. The molecular conductivities thus determined are set out in Table II.

TABLE II.

Molecular Conductivites of Quadrivalent Tellurium Compounds at 25°.

(*a*) Normal salts.

Compound. v =	256.	512.	1024.	2048.	4096.
TeMe$_3$Cl $\Lambda^{25°}$ =	*109*	*111*	*112*	(Bredig)	
,, +HCl	*512*	*516*	*517*		
α-TeMe$_2$Cl$_2$	487	507	512	519	520
,, −HCl ...	*84*	*102*	*107*	*114*	*115*
β-TeMe$_2$Cl$_2$	487	500	502	509	510
,, −HCl ...	*84*	*95*	*97*	*104*	*105*
α-TeMe$_2$Br$_2$............	495	503	511	512	513
,, −HBr	*90*	*97*	*105*	*106*	*107*
β-TeMe$_2$Br$_2$............	498	515	515	515	515
,, −HBr	*93*	*109*	*109*	*109*	*109*
α-TeMe$_2$I$_2$		505	510	514	516
,, −HI ...		*100*	*105*	*109*	*111*
β-TeMe$_2$I$_2$		504	511	526	528
,, −HI ...		*99*	*106*	*121*	*123*
TeMe$_3$I	110	112	116		

TABLE II (*cont.*).

(*b*) Hydroxy-salts.

Compound.	*v* =	256.	512.	1024.	2048.	4096.
α-$TeMe_2(OH)Cl$		103	106	108	111	111
β- ,, ...		111	117	123	127	131
α-$TeMe_2(OH)Br$ ...		107	107·5	111	114	119
β- ,, ...		113	119	126	131	132
α-$TeMe_2(OH)I$		103	107	109	111	111
β- ,, ...			122	129	133	136

(*c*) Free bases.

Compound.	*v* =	16.	32.	64.	128.	256.	512.	1024.
α-$TeMe_2(OH)_2$		1·9	2·2	2·6	2·9	3·4	4·3	6·0
β- ,, ...		33	34	35	36	37	37	

(a) *Normal salts.* The measurements recorded above showed that the equivalent conductivity of the dihalides, instead of rising to a maximum of 120 or 240, as in the case of a binary or ternary electrolyte, attained to values which exceeded 500. A precedent for these unexpected results was discovered in the molecular conductivities at 25° of the analogous alkyl derivatives of phosphorus, arsenic and antimony (Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1513), some of which are set out below for comparison with the conductivity data of Table II.

	v =	64.	128.	256.	512.	1024.
HBr		402	405	405	406	406
PEt_3Br_2		513·6	535·3	549·5	562·5	565·9
,, —HBr ...		*111·6*	*130·3*	*144·5*	*156·5*	*159·9*
$AsMe_3Br_2$		496·8	510·0	524·7	536·2	559·6
,, —HBr ...		*94·8*	*105·0*	*119·7*	*130·2*	*153·6*
$SbMe_3Br_2$		500·0	509·3	513·2	518·0	521·0
,, —HBr ...		*98·0*	*104·3*	*108·2*	*112·0*	*115·0*
	v =	80	160	320	640	1280
$SbMe_3(OH)Br$		201·2	211·8	220·6	231·2	243·9

Since all these abnormalities can be attributed to hydrolysis, we have included in Table II a series of values for the *sum* of the molecular conductivities of trimethyltelluronium chloride and hydrochloric acid, in order to show the order of magnitude of the conductivities that would be produced by complete hydrolysis of one halogen according to the equation $TeMe_2Cl_2 + H_2O \rightleftharpoons TeMe_2(OH)Cl + HCl$. For similar reasons, values are given for the observed molecular conductivities *minus* the molecular conductivity of one molecule of the halogen acid, in order to show how much of the conductivity must be attributed to the hydroxy-halide, on the supposition that one equivalent of halogen has been converted completely into hydrogen halide by hydrolysis. In these calculations, the older values for the equivalent conductivities of the halogen acids were used, since the later values depend on the use of conductivity water of higher quality than could be maintained when the solutions were heated, etc.

(b) *Hydroxy-halides.* The hydroxy-halides are not known in the solid state, since they separate from solution in the form of oxy-salts. Their existence in solution is proved by the facts that (i) when the free bases are titrated with methyl-orange or methyl-red as an indicator, only one molecule of acid is required to neutralise each molecule of base; for example, a solution of the base, which should have been $M/12{\cdot}3$ if a theoretical yield had been obtained, was found to be $N/11{\cdot}6$ when titrated with methyl-orange and $N/12{\cdot}9$ with methyl-red; (ii) the molecular conductivities of these mixed solutions bear no relationship to those of the acid and base from which they were prepared, but have the normal magnitude for a strong binary electrolyte; for example, a solution of the α-base which had been titrated with hydrobromic acid to the point of neutrality to methyl-orange gave the following conductivities:

v =	72	144	288	576	1152	2304
$\Lambda^{25°}$ =	108	112	116	119	121	124

These values have been corrected for the conductivity of the water used for dilution, but are subject to errors arising from the presence of the indicator, and of conducting impurities in the standard acid used for titration. In order to avoid these errors, the solutions for conductivity measurements were prepared by adding an equimolecular solution of the normal salt to a solution of the base which had been standardised by titration. In this way, the halogen content of the solutions was fixed by direct weighing of a crystalline salt, and any uncertainty as to the correct end-point or choice of indicator would only affect the concentration of the weak base with which the salt was mixed. The conductivities of the hydroxy-halides, prepared in this way, are set out in Table II, where they may be compared with Bredig's values for trimethyltelluronium chloride and with our own values for the iodide, $TeMe_3I$. It will be seen that the elimination of the molecule of acid, which is produced by the initial hydrolysis of the normal salts, has had very little effect on the conductivity of the hydroxy-halides, which do not appear to undergo any marked further hydrolysis even when diluted with a large volume of water.

(c) *Free bases.* These were examined in the first instance in order to determine whether they were monoacid bases like potassium hydroxide or diacid bases like barium hydroxide. It was thought that in this way the complications which had arisen from hydrolysis in the study of the normal salts might be avoided. This hope was frustrated, since the conductivities of the free bases were as much *below* those of the ordinary metallic hydroxides as those of the dihalides were *above* the conductivities of the corresponding metallic salts. The conductivities are in fact of the same order as those of a weak base like ammonia. The two bases are therefore "weak electrolytes" and not (as we had expected) analogous with the completely ionised alkalis; but we are not prepared at present to make any further statement in reference to the strength of the two bases, which we propose to investigate by electrometric methods.

The most striking feature of the preceding measurements is the steadiness of the molecular conductivities both of the normal and of the hydroxy-salts at high dilutions. The limiting value at infinite dilution, towards which the equivalent conductivities of the *normal* salts tend, is not that of *two* molecules of the halogen acid and *one* molecule of the free base (which would give a limiting value $\Lambda_{\infty}^{25^\circ} > 800$), but agrees very well with that of *one* molecule of acid with *one* molecule of the hydroxy-salt (say $\Lambda^{25^\circ} = 405 + 120$). The narrow range of molecular conductivities (from $\Lambda^{25^\circ} = 490$ to 520 at $v = 256$ to 4096) shows that, whereas the *first* halogen is hydrolysed with extraordinary ease and completeness even in the more concentrated aqueous solutions, the *second* is not hydrolysed to any appreciable extent even in the most dilute solutions. The hydrolysis of both halogens, which Vernon represented by the equation $TeMe_2I_2 + 2H_2O = TeMe_2(OH)_2 + 2HI$, does not appear to take place to any marked extent even on extreme dilution. More remarkable still is the fact that no appreciable hydrolysis occurs when the equivalent of halogen acid, which is set free in the first stage of hydrolysis, is removed from the solution. This is proved by the fact that the molecular conductivities of the hydroxy-halides tend towards a limiting value which agrees very well with that of a typical binary electrolyte, say $\Lambda^{25^\circ} = 100$ to 150, whereas, if the salt were hydrolysed in solution to one molecule of acid and one molecule of base, we should expect to find $\Lambda_{\infty}^{25^\circ} > 400$.

Molecular Structure of Quadrivalent Compounds of Tellurium.

Although the facts set out above have been established by a complete series of duplicate determinations with new materials, the interpretation to be put upon them has already become a matter of controversy, since the reading of the paper has been followed by two alternative suggestions as to the formulation of the quadrivalent compounds now under consideration. The point at issue refers to the size of the electron shell, which (including one "lone pair" of unshared electrons) would contain 10 electrons in a 4-covalent compound $[TeX_4]$, 8 electrons in a 3-covalent compound $[TeX_3]X$, and 6 electrons in a 2-covalent compound $[TeX_2]X_2$.*

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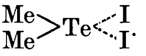
* The series need not be carried further, since the compounds now under consideration all contain two methyl groups attached to the metal.

(i) *Ten-electron shells.* Sidgwick states that tellurium "has been proved to give 4-covalent compounds in which all the groups lie in a plane" ("Electronic Theory," p. 231); but it is not obvious on what facts the "proof" of this statement depends, since quadrivalent tellurium differs from tin and lead mainly in that it does *not* form any quadricovalent compounds to correspond with tin tetraethyl or lead tetraethyl. For instance, of a series of 26 alkyl and aryl derivatives of tellurium prepared by Lederer (*Compt. rend.*, 1910, **151**, 611; *Ber.*, 1911, **44**, 2287; 1916, **49**, 1615, *et seq.*; *Annalen*, 1912, **391**, 326) not a single one contains more than three of these radicals (compare also Morgan and Burgess, this vol., p. 321). This fact provides *a priori* evidence that the expansion of the octet into a 10-electron shell * is a difficult operation, and warns us to look with suspicion on any formula in which this configuration is postulated, especially with radicals which can be ionised more readily than methyl. The fact that the trialkyltelluronium halides $[TeR_3]X$ are "strong electrolytes," like $[NMe_4]Cl$, provides further evidence that the formation of a fourth bond is resisted by the greater stability of the octet as compared with a 10-electron shell; it would indeed be unreasonable to expect that a halogen ion, which already carries a complete octet, should force its way into the complete octet of an atom of tellurium, which cannot provide an additional bond to hold a fourth alkyl group.

(ii) *Eight-electron shells.* In order to maintain the octet rule when four covalent 2-electron bonds would lead to a shell of 10 electrons, Sugden has suggested (*Chem. and Ind.*, 1927, **46**, 540) that the halogen may be held to the metal by 1-electron bonds, as in the formula  $\genfrac{}{}{0pt}{}{\mathrm{Me}}{\mathrm{Me}}\!>\!\mathrm{Te}\!<\!\genfrac{}{}{0pt}{}{\cdot\cdot\,\mathrm{I}}{\cdot\cdot\,\mathrm{I}}$. Since the evidence for these pairs of 1-electron bonds, even in the cases of phosphorus pentachloride and antimony pentachloride, rests upon a theoretical interpretation of the parachor (which has not yet been confirmed by experiment), this formula may be regarded merely as an alternative scheme for attaching both halogens to the metal to form a covalent molecule, and so enabling the salts to function as "weak electrolytes." † If, however, we wish to maintain both the duplet and the octet in this series of compounds, we are limited to a formula, $[TeMe_2X]X$, which embodies the novel

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* The formation of a 12-electron shell in sexavalent compounds such as sulphur hexafluoride and tellurium hexafluoride is not disputed; and the quadricovalency already postulated in the "sexavalent" oxy-compounds of sulphur (*Trans. Faraday Soc.*, 1923, **18**, 289), can obviously occur also in the analogous compounds of tellurium.

† For a discussion whether the small conductivity of certain salts in non-aqueous solvents is due to covalent molecules, strongly deformed ions, or ion pairs, see Ulich (*Trans. Faraday Soc.*, 1928, **24**, 27).

characteristic that, although both halogens may be ionisable in turn, only one of them can be ionised at a time. Thus, we may write the hydroxy-halides as $[TeMe_2X]OH$, in which case they would be *bases* like $[TeMe_3]OH$, or as $[TeMe_2{\cdot}OH]X$, in which case they would be binary *salts.* A given molecule could then have the structure either of a base or of a salt, and could probably exercise both functions alternately; but it could not split off a hydroxyl and a halogen ion simultaneously, except by forming an unstable 6-electron shell.

(iii) *Six-electron shells.* Finally, the dihalides may be regarded as salts of a diacid base, and formulated as $[TeMe_2]X_2$. This is the most plausible way of expressing Vernon's statement that " both atoms of halogen are ionisable," although (as was natural at the time when his papers were published) he did not make any distinction between polar and non-polar bonds.

(a) *Hydroxy-halides.*—In discussing the molecular structure of this series of compounds, it is convenient to consider first the α-hydroxy-halides on account of the very close analogies which they present with the trimethyltelluronium halides.

(i) The hydroxy-halides behave as *neutral* salts which, prepared as described above, are not hydrolysed to any large extent, even at the highest dilutions.

(ii) They also behave as *strong electrolytes.* For example, whereas the chloride, $TeMe_3Cl$, gives $\Lambda^{25^\circ} = 103$ to 112 at $v = 64$ to 1024, and the iodide, $TeMe_3I$, gives $\Lambda^{25^\circ} = 110$ to 116 at $v = 256$ to 1024, the three α-hydroxy-halides give values for Λ^{25° ranging from 103 to 119 at $v = 256$ to 4096. The conductivities of the salts also appear to be additive functions of those of their ions, since they can be interpreted on the assumption that the ion $[\alpha\text{-}TeMe_2{\cdot}OH]^+$ has a mobility of about the same magnitude as $[TeMe_3]^+$, the slightly higher conductivity of the bromide being in agreement with the slightly greater mobility of the bromide ion as compared with the chloride and iodide ions.

(iii) This additive relationship also extends to the *colour* of the solutions, since the striking contrast which exists between the absorption spectra of the unhydrolysed dihalides, when examined in alcoholic solutions, disappears when these compounds are hydrolysed to the corresponding hydroxy-halides by dissolution in water. In particular, the " iodoform band," which distinguishes the di-iodides from the dibromides and dichlorides, is entirely lacking in the case of the α-hydroxyiodide, which gives only a general absorption ($\log \varepsilon = 2{\cdot}5$ at 2600 Å.) of about the same intensity as that of the dichlorides.

The β-hydroxy-halides also behave as *strong electrolytes* and *neutral salts,* which do not undergo any marked hydrolysis in solution. The slightly higher conductivities of the β-salts shown in Table II cannot be attributed to unequal mobility of the kations $[\alpha\text{-TeMe}_2\cdot\text{OH}]^+$ and $[\beta\text{-TeMe}_2\cdot\text{OH}]^+$, since this difference should appear also in the conductivities of the hydrolysed normal salts. We suspect that it may depend on some small difference in the end-point when two weak bases of unequal strength are being titrated; but this difference is not large enough to affect any of the arguments that are used in the present paper. Since, therefore, both series of hydroxy-halides behave as neutral, strong electrolytes, we have no hesitation in assigning to them the general formula * $[\overset{+}{\text{T}}\text{eMe}_2\cdot\text{OH}]\overset{-}{\text{X}}$.

(b) *Dihalides.*—The study of the dihalides is rendered difficult by the fact that they are hydrolysed almost completely by water, even when an excess of free acid is present; it has therefore been impracticable to determine the conductivity of the unhydrolysed salt by Schilow's method of using a dilute acid as solvent. As we have no direct knowledge of the conductivity of the dihalides in aqueous solutions, we can only speculate that, since no important change of conductivity is produced when CH_3 is replaced by OH (although this involves the replacement of a "positive" by a "negative" radical), the further replacement of OH by Cl, Br or I would not be likely to alter the conductivity in any fundamental way; in particular, the introduction of a second easily ionised radical would not be likely to impede the ionisation of the salt to such an extent as to convert the strong electrolyte into a weak electrolyte or a non-electrolyte, if it could be examined in water in an unhydrolysed state. Mere analogy therefore suggests that the dihalides should be formulated after the model of the trimethyl- and hydroxy-halides, as $[\text{TeMe}_2\text{X}]\text{X}$; this is also in harmony with the formulation of the α-tetraiodide as $[\text{TeMe}_2\text{I}]^+\text{I}_3^-$.

This unsymmetrical formula is the only one which will account simultaneously for the colour of the salts and for their conductivity in a medium such as acetonitrile; but, if *two* formulæ are assigned to each compound, it is obviously possible to use the 10-electron formula to account for the colour, and the 6-electron formula to account for the ionisation of the dihalides; or we may postulate a dynamic equilibrium between the form represented by the unsymmetrical octet formula, $[\text{TeMe}_2\text{X}]\text{X}$, and a valency-isomeride represented by Sugden's symmetrical octet formula. These alternative hypotheses, however, all involve an increase in the number of

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* It is, however, possible that the neutral hydroxyl groups may give rise even in aqueous solution, to oxides similar to those which are formed when the solutions are evaporated to dryness.

arbitrary variables that are used to express the behaviour of the salts and we are not yet convinced that this is necessary. Thus the hypothesis that both halogens are ionisable simultaneously could only be justified by evidence, which we have not yet found, that the salts (or the bases from which they are derived) can behave as ternary electrolytes; and, although the dissimilar behaviour of the two halogens towards water does not afford positive proof of the unsymmetrical formula (since a similar contrast exists between the behaviour of two halogens in $\alpha\alpha'$-dibromocamphor, where no difference of linkage need be suspected), it is nevertheless of vital importance, because, if no more contrast had been found than that which exists between the two halogens of calcium chloride or methylene iodide, there would be no justification for placing one atom inside the bracket and the other outside. Actually, however, the contrast is quite as well marked as in many of the co-ordination compounds in which this distinction is made. Whilst, therefore, we are ready to admit the possible validity under various conditions of the symmetrical formulæ of Sidgwick, Sugden, and Vernon, we feel free to regard them as still unproved.

(c) *Bases.*—In contrast to the dihalides and the hydroxy-halides, the free bases are very poor conductors. The reversibility of their ionisation can, however, be explained quite readily, as in the case of ammonia, either by the formation of anhydrides, such as is already known to occur in the case of the hydroxyhalides, thus $[\overset{+}{\mathrm{T}}\mathrm{eMe_2{\cdot}OH}]\overset{-}{\mathrm{O}}\mathrm{H} \rightleftharpoons [\overset{+}{\mathrm{T}}\mathrm{eMe_2}\overset{-}{\mathrm{O}}] + \mathrm{H_2O}$, or by the co-ordination of the hydroxyl ion with an atom of hydrogen inside the bracket. The formation of a 4-covalent compound $[\mathrm{TeMe_2(OH)_2}]$ is another alternative, which we should hesitate to adopt until some independent proof is available of the existence of 4-covalent derivatives of quadrivalent tellurium.

Summary.

(*a*) Measurements have been made of the extinction coefficients and molecular conductivities of Vernon's dimethyltelluronium dihalides. The close resemblance which Vernon observed between the α- and β-compounds is confirmed by these observations.

(*b*) The α- and β-dichlorides show only general absorption, but the dibromides show a marked step-out; the α- and β-di-iodides show the twin maxima already recorded for iodoform and potassium tri-iodide. These two maxima also appear, with an enhanced intensity, in the α-tetraiodide, to which the formula $[\overset{+}{\mathrm{T}}\mathrm{eMe_2I}]\overset{-}{\mathrm{I_3}}$ is assigned. The spectroscopic evidence indicates that a similar formula may be assigned to the dihalides.

(*c*) Instead of behaving as binary or ternary electrolytes in aqueous solution, the dihalides give conductivities which indicate that one halogen atom is hydrolysed more or less completely and the other atom forms a halogen ion, *e.g.*, $\overset{+}{[\text{TeMe}_2\text{Cl}]}\overset{-}{\text{Cl}} + \text{H}_2\text{O} \rightleftharpoons \overset{+}{[\text{TeMe}_2\cdot\text{OH}]}\overset{-}{\text{Cl}} + \overset{+}{\text{H}}\overset{-}{\text{Cl}}$. The hydroxy-halides produced by this hydrolysis are strong electrolytes which are not hydrolysed to any large extent even when the equivalent of acid shown in the preceding equation is removed. The free bases, on the other hand, which can be prepared only with the help of silver oxide, are weak electrolytes, like ammonia.

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