

CCLXX.—*Studies of Valency. Part XIII. Further Experiments on the Molecular Structure of the Quadrivalent Derivatives of Tellurium.*

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IN the following paper the properties of the quadrivalent derivatives of tellurium are reviewed in the light of the structures assigned by Drew (this vol., p. 560) to Vernon's α - and β -dimethyltelluronium dihalides and to the bases from which they are derived. Most of the experiments were made before we had access to the manuscript of Drew's paper, but the later stages of the work were carried out

in correspondence with him and, in part, with materials which he very kindly placed at our disposal. Our observations are entirely in accord with Drew's principal conclusion, that the conversion of the α - into the β -dihalides involves the wandering of a methyl group from one atom of tellurium to another, and on this basis we have been able to account for a number of anomalies for which no adequate explanation had hitherto been given, *e.g.*, the contrast in colour between the α - and β -salts, the anomalous conductivity data of the β -base, and the inflected curves obtained by electrometric titration of this base. We have also been able to verify Drew's conclusion by colorimetric measurements of the dihalides prepared by synthesis and by molecular rearrangement, and moreover to extend it to the corresponding compounds of the ethyl series, from which we have separated specimens of the *monoethyltri-iodide*, TeEtI_3 , and of the triethyl monobromide and monoiodide, TeEt_3Br and TeEt_3I .

We also concur in Drew's opinion that the β -salts "are correctly represented by the general formula $\text{Me}_3\text{Te}^+ \dots \bar{\text{Te}}\text{MeX}_4$, equivalent to the co-ordination formula $[\text{Me}_3\text{Te}]\text{TeMeX}_4$, in which all the halogens and alkyl groups are covalently linked to tellurium"; but we think that he has laid undue stress on the contrast between the physical properties of the α - and β -dihalides, which have formed the subject of our own recent investigations. Support for his statement that the α -dihalides "are broadly non-polar in character," but that the β -dihalides "are complex substances of salt-like character, having the same empirical formula" can be obtained from the data now recorded for the conductivities of the bromides and iodides in acetonitrile. The contrast, however, is only one of degree, and further evidence is needed before we should feel justified in concluding that the conducting molecules of the β -salts are necessarily complex whilst those of the α -salts are always monomeric. In any case the contrast between the "broadly non-polar" α -compounds and the "salt-like" β -compounds of the dimethyl series (which we failed to observe when experimenting with these substances over a period of two years) is obviously not applicable to the corresponding compounds of the diethylseries, where both dichlorides and both dibromides are liquids whilst both di-iodides are solids.

Finally, we wish to put on record the view that, whilst Drew has finally disproved the supposed stereoisomerism of the α - and β -compounds, the title of his paper, in so far as it implies that the α -compounds cannot exist in dimeric forms, is still unjustified. In particular, since the complex salts of the β -series evidently dissociate very easily into their components, especially in the case of

the liquid ethyl compounds, we are unwilling at the present stage to rule out the possibility that crystallisation of the *like* molecules of an α -dihalide, e.g., TeMe_2I_2 , may give rise to a complex of similar type to (although of less stability than) those formed by the *unlike* molecules, e.g., TeMe_3I and TeMeI_3 , of a "dihalide" of the β -series.

Although this view cannot yet be fully proved, since X-ray analysis of the crystals has shown that their structure is more complex than we had anticipated, it is nevertheless supported very strongly by the data, already given by Vernon and Knaggs (J., 1921, **119**, 105), for the two iodides, which are as follows :

	System.	Axial ratios, $a : b : c$.	Axial angle, β .	d_4^{14} .
α	Monoclinic holohedral	0.5578 : 1 : 0.4310	$72^\circ 21'$	3.338
β	„ „	0.5465 : 1 : 0.4222	$76^\circ 52'$	3.305

"The similarity of the two forms is so close that they stand to one another much in same relation as the members of an isomorphous series" (*idem, ibid.*). The morphotropic relations are therefore already sufficient to justify a belief in the general similarity of structure of the two solid compounds, but we are informed that their equality of density makes it almost impossible to accept the contention that one compound consists of non-polar molecules whilst the other has a salt-like or ionic lattice, since in the latter case the properties of the crystal would be modified profoundly by the electrostatic forces between the ions. The *a priori* evidence is therefore strongly in favour of the view that the solid phase of the α -compounds may have a structure of similar type to that assigned by Drew to the β -compounds.

This conclusion also makes it possible to provide a plausible interpretation of two additional phenomena for which no clear explanation has yet been given. In the case of the β -compounds, the solid phase may be either a complex salt, $[\text{TeMe}_3]^+[\text{TeMeI}_4]^-$, or a mere aggregate or "double salt" of the two components, which we can represent as $\text{TeMe}_3\text{I}, \text{TeMeI}_3$. In the complex formula all the atoms are "covalently linked to tellurium" and may be expected to contribute to the colour of the complex ion, but in the double salt one of the iodine atoms should be colourless as in TeMe_3I ; moreover, a concentration of halogen atoms on a single carbon atom is known to produce a disproportionately great effect on the absorption. The existence of a labile red and a stable purple solid form of the bromotri-iodide, $\text{TeMe}_3\text{Br}, \text{TeMeI}_3$ or $[\text{TeMe}_3]^+[\text{TeMeBrI}_3]^-$ (Drew, *loc. cit.*), could therefore be explained by formulating the red crystals as the "double salt" and the purple crystals as the "complex salt." In the same way, the existence of an orange high-temperature form and a purple low-temperature form of *cyclotelluripentane* di-iodide (Morgan and Burgess, J., 1928, 321),

which cannot be explained by any mere rearrangement of the lattice, and must therefore be attributed to some change of molecular structure, could be accounted for if the stable phase at low temperatures were a dimeric complex salt, *e.g.*, $[\text{C}_5\text{H}_{10}\text{TeI}]^+[\text{C}_5\text{H}_{10}\text{TeI}_3]^-$, which was dissociated at higher temperatures into a monomeric form. The facts that both forms yield identical yellow solutions, and that the crystals are interconvertible, although without a well-defined transition temperature, are in accord with the usual characteristics of reversible changes of this type.

The incomplete character of some of the data now recorded is inevitable in view of the properties of the dialkyltellurides and their derivatives, which are so objectionable that experimental work can only be undertaken intermittently and on a limited scale. For this reason, we do not propose to undertake any further work with these simple derivatives, and are now confining our attention to an attempt to resolve some of the aryl derivatives into optically active components.

EXPERIMENTAL.

1. Absorption Spectra.

Fig. 1 (see also Table I) shows the molecular extinction coefficients of two simple trihalides and four double or complex salts prepared by Drew. The coefficients of Drew's " β -dihalides" are shown by full lines in comparison with broken lines showing the values of the " β -dibromide" and " β -di-iodide" prepared by Vernon's method; to prevent overlapping, the molecular extinction coefficients for these two pairs of curves are plotted for *one atom of tellurium* as in Vernon's formulæ for the β -salts. The agreement of the full and broken curves provides quantitative evidence of the identity of the " β -salts" prepared by synthesis and by molecular rearrangement.

The tribromide, TeMeBr_3 , which has not been examined previously, resembles the " β -dibromide" (J., 1928, 310) in showing only a "step-out" in the ultra-violet, but this is not so well-defined and occurs at an intensity which is about 6 times less than in the dimeric " β -dibromide"; on the other hand, the tribromoiodide, $\text{TeMe}_3\text{I}, \text{TeMeBr}_3$, which is eight times more absorbent in the visible region than the simple tribromide, gives indications of a second step-out, which is perhaps an early stage in the development of the twin maxima of the iodoform band (J., 1926, 622). These are developed fully in the bromotri-iodide, $\text{TeMe}_3\text{Br}, \text{TeMeI}_3$, as well as in the tri-iodide, TeMeI_3 , the curve for which is practically identical throughout with that for the " β -di-iodide" when the values for the latter compound are doubled to correspond with Drew's formula for this salt. The fourth atom of iodine in the dimeric " β -di-iodide" therefore produces no increase of absorptive power as compared

with the simple tri-iodide, but this result could be explained by the dissociation of the complex in these very dilute alcoholic solutions.

FIG. 1.

Molecular extinction coefficients of synthetic β -salts. (In order to avoid overlapping, the values for β -TeMe₂Br₂ and β -TeMe₂I₂ are plotted for one atom of tellurium.)

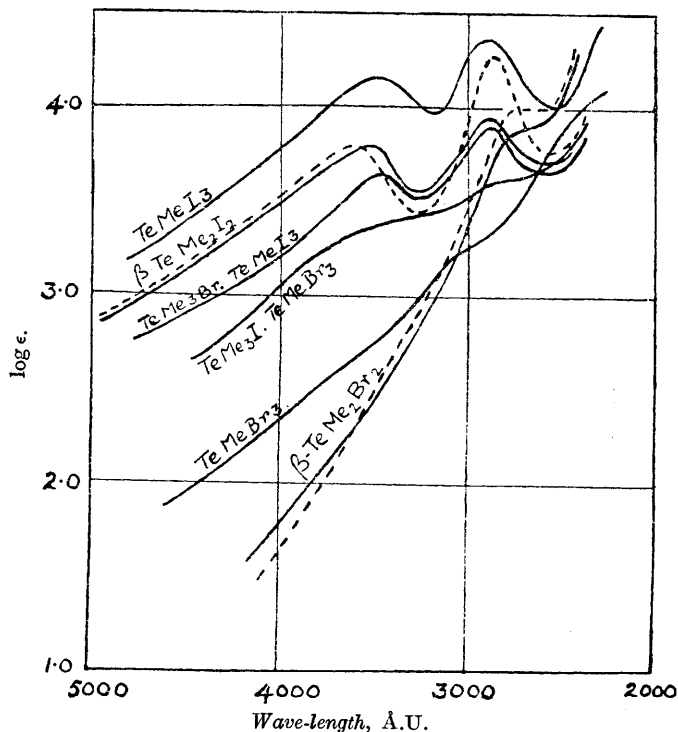


TABLE I.

Molecular Extinction Coefficients of the β -Dihalides.

(a) *Selective absorption.*

	Maxima.
TeMeI ₃	log ϵ = 4.14 at 3500 Å.U.; log ϵ = 4.37 at 2900 Å.U.
β -TeMe ₂ I ₂ :	
{ "Vernon's" }	log ϵ = 3.80 at 3630 Å.U.; log ϵ = 4.25 at 2860 Å.U.
{ Synthetic }	log ϵ = 3.79 at 3550 Å.U.; log ϵ = 3.95 at 2880 Å.U.
TeMe ₃ Br ₂ , TeMeI ₃	log ϵ = 3.64 at 3480 Å.U.; log ϵ = 3.90 at 2890 Å.U.
β -TeMe ₂ Br ₂ :	
{ "Vernon's" }	Step out : log ϵ = 4.0 from 2780 to 2560
{ Synthetic }	Step-out : log ϵ = 3.9 from 2800 to 2600

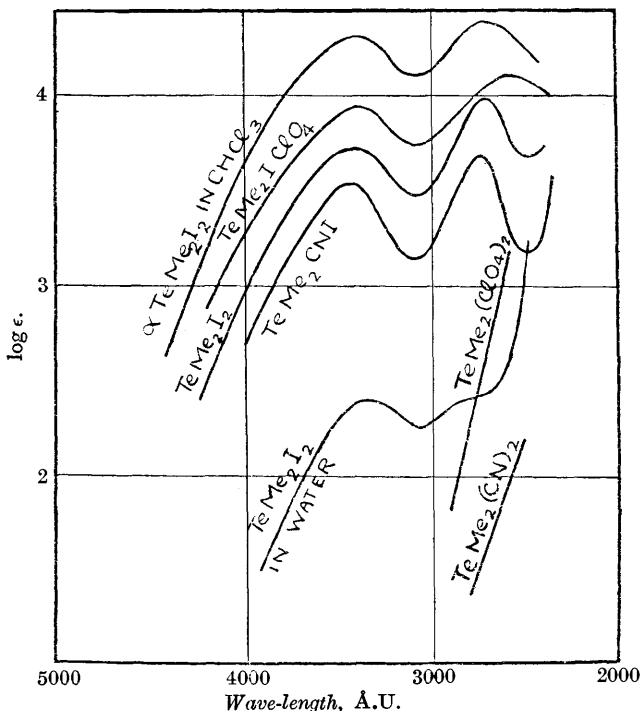
(b) *General absorption.*

	λ =	4000.	3500.	3000.	2500.
TeMe ₃ I ₃ , TeMeBr ₃	log ϵ =	3.06	3.37	3.53	3.76
TeMeBr ₃	log ϵ =	2.34	2.75	3.27	3.88

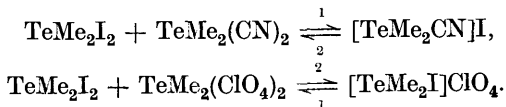
Fig. 2 shows the results of a series of experiments designed to test the semi-polar formula which we have assigned to the dihalides (J., 1928, 319). We anticipated that a mixture of iodide and cyanide would form a mixed salt of the type $[\text{TeMe}_2\text{CN}]\text{I}$, which would be colourless like the hydroxyiodide, $[\text{TeMe}_2\text{OH}]\text{I}$, but that a mixture of iodide and perchlorate would form a mixed salt of the type $[\text{TeMe}_2\text{I}]\text{ClO}_4$, in which the colour of the di-iodide would not only be retained but would be intensified because each molecule would yield

FIG. 2.

Molecular extinction coefficients of mixed salts (in alcohol).



two molecules of the coloured iodo-perchlorate. The results, which are set out in Table II and plotted in Fig. 2, show that the extinction coefficient at 3440 \AA.U. of an alcoholic solution of the di-iodide was *decreased* by about 34% when mixed with an equivalent quantity of the dicyanide, but *increased* by about 66% when mixed with an equivalent of perchlorate. The reactions may therefore be expressed as



α -Dimethyltelluronium diperchlorate, $\text{TeMe}_2(\text{ClO}_4)_2$, prepared by mixing a solution of the α -base with 2 equivs. of perchloric acid, evaporating the solution to a syrup, and crystallising it in a vacuum desiccator, separated in colourless crystals, m. p. 37° [Found, by conversion into di-iodide : TeMe_2I_2 , 124. $\text{TeMe}_2(\text{ClO}_4)_2$ requires TeMe_2I_2 , 125.5%].

α -Dimethyltelluronium dicyanide, $\text{TeMe}_2(\text{CN})_2$, was prepared by acting upon the iodide with silver cyanide; the solution was evaporated in a vacuum desiccator, and the cyanide separated in colourless needles, m. p. 90° [Found, by conversion into di-iodide : TeMe_2I_2 , 193. $\text{TeMe}_2(\text{CN})_2$ requires TeMe_2I_2 , 196%].

TABLE II.

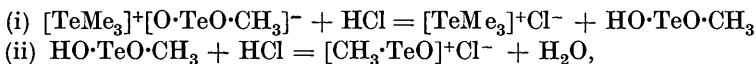
Molecular Extinction Coefficients of Perchlorate, Cyanide, and Mixed Salts.

Salt.	Solvent.	Maxima.
α - TeMe_2I_2	Chloroform	$\log \epsilon = 4.33$ at 3400; $\log \epsilon = 4.40$ at 2720
α - $\text{TeMe}_2\text{I}(\text{ClO}_4)$	Alcohol	$\log \epsilon = 3.94$ at 3440; $\log \epsilon = 4.12$ at 2560
α - TeMe_2I_2	Alcohol	$\log \epsilon = 3.72$ at 3440; $\log \epsilon = 4.00$ at 2720
α - $\text{TeMe}_2(\text{CN})\text{I}$	Alcohol	$\log \epsilon = 3.54$ at 3420; $\log \epsilon = 3.70$ at 2740
α - TeMe_2I_2	Water	$\log \epsilon = 2.40$ at 3330
General absorption.		
α - $\text{TeMe}_2(\text{ClO}_4)_2$	Alcohol	$\log \epsilon = 1.36$ at 2800 to $\log \epsilon = 2.20$ at 2500
α - $\text{TeMe}_2(\text{CN})_2$	Alcohol	$\log \epsilon = 1.8$ at 2900 to $\log \epsilon = 3.20$ at 2580

2. Conductivities.

(a) *In Water.*—In Fig. 3, we have plotted, against the square root of the concentration, the values already recorded (J., 1928, 1998, 3186) for the conductivities of the “ β -bases” of the dimethyl and diethyl series. It will be seen that the dimethyl base, unlike the diethyl base, gives an approximately linear relation between Λ and \sqrt{c} , and therefore behaves as a strong electrolyte, but with a limiting conductivity $\Lambda_0 = ca. 37$ only. If, however, we make use of Drew’s dimeric formula, the limiting conductivity, $\Lambda_0 = 74$, becomes comparable with that of a binary salt, such as trimethylammonium acetate, for which $\Lambda_0 = 50 + 40 = 90$, or triethylammonium propionate, for which $\Lambda_0 = 34.6 + 36.4 = 71$. We therefore regard Vernon’s β -base as the trimethyltelluronium salt of Drew’s telluracetic acid and assign to it the complex formula $[\text{TeMe}_3]^+[\text{O}\cdot\text{TeO}\cdot\text{CH}_3]^-$. A simple calculation, based upon the p_H of the solution, then shows that this salt is hydrolysed to the extent of only 0.06% at a concentration of $M/32$, and that only 0.2% of its conductivity is due to hydroxyl ions. On the same basis, we can also interpret the inflected curves which we obtained in the electro-

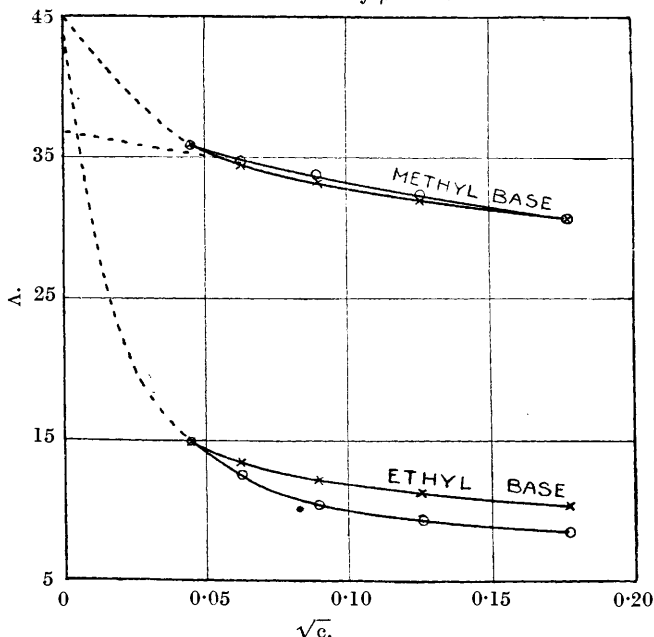
metric titration of the β -base (J., 1928, 2003) as due to the two consecutive reactions



where the amphoteric telluracetic acid of equation (i) behaves as a univalent base in equation (ii).

Finally, in order to account for the fact that the β -dihalides, in spite of their more complex structure, are hydrolysed to the same

FIG. 3.
Conductivities of β -bases.



The broken lines indicate possible values of Λ_0 .

extent and have almost the same conductivity in water as the α -dihalides, we have measured the conductivity in a series of aqueous solutions of Drew's monomethyl tribromide and tri-iodide. The results set out below are in good agreement with the equation

	v	= 151	256	512	1024	2048	4096
$\text{TeMeBr}_3 \Lambda^{25^\circ}$	=			989	996	1001	1003
$\text{TeMeI}_3 \Lambda^{25^\circ}$	=	975	979	983	987	992	998

$\text{TeMeX}_3 + \text{H}_2\text{O} = [\text{TeMeO}]\text{X} + 2\text{HX}$, which requires a limiting conductivity of about $40 + 75 + 2 \times 425 = 965$, on the assumption that "telluracetyl bromide" and "telluracetyl iodide" are strong

binary electrolytes and are not hydrolysed to any marked extent in solution. The slightly higher values recorded experimentally cannot be attributed to hydrolysis of these monohalides, since the conductivities are almost independent of the dilution, but they may be due to the formation of a condensed kation of higher mobility, comparable with the condensed kation of the crystalline oxyiodide $I[TeMe_2 \cdot O \cdot TeMe_2]I$.

(b) *In the Fused State*.—The measurements of conductivity hitherto published refer exclusively to aqueous or aqueous-alcoholic solutions, in which the dihalides are hydrolysed almost completely to oxy- or hydroxy-halides. In order to remedy this defect we have measured the conductivity of some typical halides in the fused state and in non-aqueous solutions (see below). With one exception, marked with an asterisk, the specific conductivities of the fused salts were measured in a vessel with a cell constant of 9.42 cm.⁻¹. The other vessel, which had a cell constant of only 0.000457, had been designed for measurements of specific inductive capacity, but the conductivity of the liquid was too great to enable us to measure the dielectric constant of the molten salt. The results were :

- (i) α - $TeMe_2Cl_2$, m. p. 97°. Fused, $\kappa = 3 \times 10^{-5}$ at 105°.
Solid, $\kappa = 7 \times 10^{-6}$ at 0°.
- (ii) α - $TeEt_2I_2$, m. p. 57°. *Fused, $\kappa = 4.6 \times 10^{-4}$ at 68°; 2.9×10^{-4} at 64°.
Solid, $\kappa = 4 \times 10^{-5}$ at 0°.

Biltz (*Z. anorg. Chem.*, 1924, **133**, 312; 1926, **152**, 267) found that the fused chlorides of metals fell into two groups, the specific conductivities at the melting point being 10^{-1} or 10^{-6} approximately. A few chlorides (*e.g.*, $BeCl_2$ and Hg_2Cl_2) had intermediate conductivities, and it is clear that the α -dialkyltelluronium dihalides must be classed with these.

(c) *In Non-aqueous Solvents*.—The specific conductivities of some typical α - and β -dihalides in methyl alcohol, acetonitrile, benzonitrile, and chloroform (of specific inductive capacities, 31, 39, 26, and 5, respectively) are set out in Table III. For the sake of comparison the tercovalent oxyiodide, $I[TeMe_2 \cdot O \cdot TeMe_2]I$, has also been examined in methyl alcohol and in chloroform.

(i) Methyl alcohol was purified by the method of Hartley and Raikes (*J.*, 1925, **127**, 524). The first sample ($\kappa = 0.5 \times 10^{-6}$ at 25°) was comparable with that used by Hartley and Frazer (*Proc. Roy. Soc.*, 1925, *A*, **109**, 311), but the conductivity of the second sample could not be brought below 1.9×10^{-6} . The alcohol was always used immediately after distillation, since its conductivity increased on keeping. The molecular conductivities of the salts are plotted against the square root of the concentration in Fig. 4, with values potassium iodide calculated from Hartley's formula. The

TABLE III.

Molecular Conductivities of α - and β -Dialkyltelluronium Dihalides in Non-aqueous Solvents at 25°.(i) *Methyl alcohol.*

	$v = 32$	64	128	256	512	1024	2048	4096
KI (Hartley)		82.2	91.7	98.5	103.3	106.6	109.0	110.6
* α -TeMe ₂ OI ₂			48	64	82	102	120	133
* α -TeMe ₂ I ₂	2.9	4.3	6.7	10	16	26	41	63
† α -TeMe ₂ Br ₂	§8.0	9.6	14.4	22	34	54	84	126
† β -TeMe ₂ I ₂				64	80	107	146	198
† β -TeMe ₂ Br ₂		81.5	93	121	153	192	230	251

* Solvent had $\kappa = 0.5 \times 10^{-6}$.† Solvent had $\kappa = 1.9 \times 10^{-6}$.

‡ These numbers probably refer to products of interaction with the solvent.

§ At $v = 41.7$.|| At $v = 90$.(ii) *Acetonitrile.*

							Λ_{∞}	
* α -TeMe ₂ I ₂				2.4	5.1	8.2	12	—
† α -TeMe ₂ Br ₂			3.2	4.6	6.4	9.3	13.9	—
† β -TeMe ₂ I ₂				66.4	70.2	72.6	74	(79)
† β -TeMe ₂ Br ₂	‡63.7	70.8		74.1	77.2	79.2	80.7	(84)

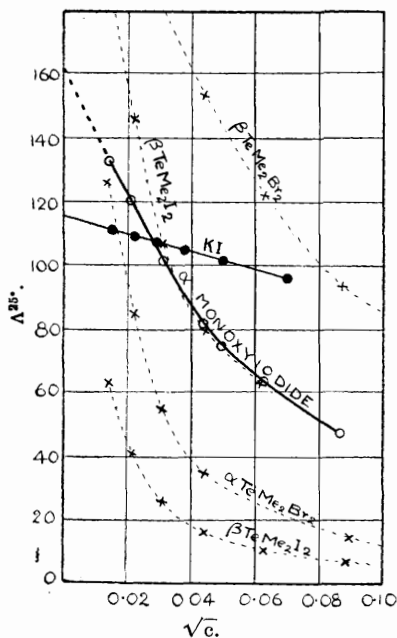
* Solvent had $\kappa = 1.5 \times 10^{-6}$.† Solvent had $\kappa = 2.8 \times 10^{-6}$.‡ At $v = 76$.(iii) *Benzonitrile, $\kappa = 1.1 \times 10^{-6}$.* α -TeMe₂I₂ $v = 183, \Lambda = 0.71$.(iv) *Chloroform, $\kappa = 0.1 \times 10^{-6}$.* α -TeMe₂I₂ $v = 7.5, \Lambda = 0.0015$. α -(TeMe₂)₂OI₂ $v = 64, \Lambda = 0.0026$.

tercovalent oxyiodide, I[TeMe₂·O·TeMe₂]I, behaves as a ternary electrolyte, its molecular conductivity being substantially greater than that of potassium iodide at concentrations less than $M/1000$; extrapolation gives $\Lambda_0^{25^\circ} = 162$ approx., from which we may subtract 2×61 for the two iodide ions, leaving about 40 units for the mobility of the kation. The molecular conductivities of the α - and β -dihalides, on the other hand, attain values which are much higher than those deduced by assigning to the ion [TeMe₂I]⁺ or [TeMe₂Br]⁺ the same mobility as [TeMe₂·O·TeMe₂]⁺⁺, e.g., $\Lambda_0^{25^\circ} = 40 + 61 = 101$. Since every available precaution was taken to dry the alcohol, in view of the known risk of hydrolysing these salts in presence of a mere trace of water, we suspect that there may have been a definite interaction with the solvent, just as there must be when an ester is saponified with sodium methoxide in anhydrous methyl alcohol, e.g., TeMe₂I₂ + MeOH = [TeMe₂OMe]I + HI, compare C₆H₅·CO₂Me + KOMe = C₆H₅·CO₂K + Me₂O. In this connexion it may be noted that Vernon (J., 1920, **117**, 897) postulated the formation of a dimethoxy-compound, TeMe₂(OMe)₂, as a product of distillation of the " β -base."

(ii) Acetonitrile (which cannot be purified with phosphoric oxide) was dried with fused calcium chloride and fractionally distilled

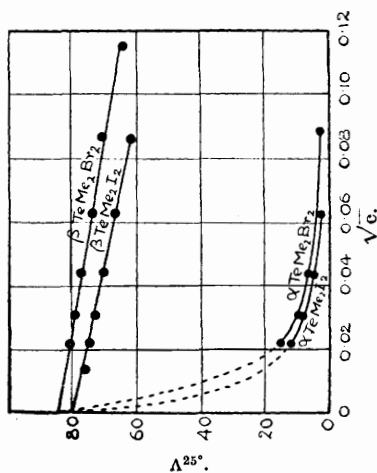
three times over a range of 0.05° . In Fig. 5 the molecular conductivities of the α - and β -dimethyltelluronium dibromides and di-iodides have been plotted against the square root of the concentration. The β -salts show a linear relation between Λ and \sqrt{c} , and extrapolation gives $\Lambda_0^{25^\circ} = 79$ and 84 for the bromide and iodide respectively. These values, which refer to a single atom of tellurium, are similar to those observed in solutions of silver nitrate and of sodium iodide, both of which give $\Lambda_0^{25^\circ} = 160$ in acetonitrile. The

FIG. 4.



Molecular conductivities in methyl alcohol.

FIG. 5.



Molecular conductivities in acetonitrile.

α -salts, on the other hand, give very much lower values and are obviously behaving as weak electrolytes. The oxyiodide was not examined, since it gave a white precipitate, readily soluble in water, and a yellow solution which may have contained the di-iodide.

(iii) Benzoinitrile was purified by Martin's method (J., 1928, 3275) and had a specific conductivity $\kappa = 1.1 \times 10^{-6}$. The α -di-iodide is a poor conductor in this solvent, but no measurements were made of the β -salt.

(iv) Chloroform was purified by being shaken with calcium chloride to remove alcohol and water, and then carefully fractionated.

The conductivity of the α -di-iodide is very small, but is similar to that of the oxyiodide, which behaves as a strong electrolyte in water.

3. Solubilities.

The following table shows the approximate weight of α -dimethyl-telluronium di-iodide dissolved by 10 c.c. of various organic solvents at 25°.

Acetone	0.997 g.	Acetonitrile	0.521 g.
Benzene	0.709 g.	Ethyl alcohol	0.218 g.
Chloroform	0.551 g.	Carbon tetrachloride ...	0.058 g.
	(Increasing rapidly with temperature.)	cycloHexane	0.01 g.

4. Parachors.

Diphenyl telluride, for a sample of which we are very greatly indebted to Mr. W. H. Mills, was dried with fused calcium chloride, and distilled at 190°/15 mm. The densities and surface tensions were measured at 19°, 32°, and 58°, capillaries of radius 0.4765 and 0.2177 mm. being used; these measurements gave a mean value $[P] = 457.4$, of which 380 units can be assigned to the two phenyl groups, leaving a residue for one atom of tellurium of 77.4 ± 1.0 .

Of the six dihalides studied by Vernon, the α -dichloride is the only one with which measurements of the parachor could be made, and even here there is only a very narrow margin between the melting point at 97° and the temperature of decomposition (which is rapid above 110°). Eight measurements at 105° showed a mean deficiency of 15.8 units as compared with the value for bivalent tellurium in diphenyl telluride.

The dihalides of the diethyl series melt at much lower temperatures, so that there is less risk of decomposition. The fused α -di-iodide showed a mean deficiency of 24.7 units at 67–78°, and the liquid “ β -dibromide” at 0° and at 22.8° showed a mean deficiency of 26.4 units on each atom of tellurium.

The observations on the dimethyl dichloride may perhaps be questioned, since they show a deficiency of only 16 instead of the expected 26 units, as in the α - and β -diethyl compounds; but there was no obvious difference between them, except the higher temperature at which the fused methyl compound was examined.

The experimental data are given in Table IV, the surface tension, γ , having been determined by the method of capillary rise.

5. Analysis and Synthesis of “ β -Dihalides” of the Diethyl Series.

Drew separated the “ β -dihalides” of the methyl series into their component salts by making use of the unequal solubilities in water of the trimethyl bromide or iodide and the monomethyl hydroxide,

TABLE IV.

*Parachors.**Diphenyl telluride, Te(C₆H₅)₂.*

Densities (determined with silica floats calibrated in mixtures of bromoform and toluene): $d_4^{19^\circ}$ 1.601, $d_4^{32^\circ}$ 1.582, $d_4^{58^\circ}$ 1.543.

Kraft and Lyons (*Ber.*, 1894, 27, 1768) give $d_4^{20^\circ}$ 1.574, $d_4^{15.2^\circ}$ 1.556.

At 19° :	γ =	45.4	45.3	45.4	46.0	45.4
	[P] =	456.4	456.4	456.4	458	456.4
At 32° :	γ =	43.6	43.6	43.9	43.5	
	[P] =	457.2	457.2	457.8	457.2	
At 58° :	γ =	40.6;	[P] =	460.7.		

Mean of 10 values, [P] = 457.4. $\text{Te} = 457.4 - 380.0 = 77.4 \pm 1.0$.

 α -Dimethyltelluronium dichloride, TeMe₂Cl₂, m. p. 97°.

$d_4^{105^\circ} = 2.102$ (determined in a density bottle of 2 c.c. capacity suspended in a boiling salt solution).

At 105° :	γ =	43.7	45.4	45.6	47.0	46.9	47.3	45.6	44.7
	[P] =	279.4	281.9	282.3	284.4	284.2	284.7	282.3	280.8

Mean of 8 values, [P] = 282.5. $\Sigma[P] = 298.3$. Deficiency = 15.8.

 α -Diethyltelluronium di-iodide, TeEt₂I₂, m. p. 57°.

$d_4^{73^\circ} = 2.707$, $d_4^{70^\circ} = 2.715$, $d_4^{67^\circ} = 2.720$, $d_4^{60^\circ} = 2.732$.

$t =$	67°	67°	67°	60°	70°	78°	78°	78°
$\gamma =$	49	46.8	47.7	47.3	45.9	45.3	49.3	50.2
[P] =	427.4	422.3	423.8	421.6	421.2	421.3	430.0	432.0

Mean of 8 values, [P] = 425.0. $\Sigma[P] = 449.7$. Deficiency = 24.7.

 β -Diethyltelluronium dibromide, TeEt₃Br, TeEtBr₃ or (TeEt₃)TeEtBr₄.

Density of liquid (determined in a density tube with a capacity of 0.2 c.c.):

$d_4^{20^\circ} = 2.420$, $d_4^{22.3^\circ} = 2.360$.

At 0° :	γ =	44.8	44.7	44.1
	[P] =	378.7	378.6	377.1
At 22.8° :	γ =	48.5	49.2	47.3
	[P] =	376.8	378.1	374.5

Mean of 6 values, [P] = 377.3. $\Sigma[P] = 403.7$. Deficiency = 26.4.

i.e., TeMe₃Br or TeMe₃I and Me·TeO·OH. The separation of the "β-dihalides" of the diethyl series into their component simple salts is more difficult, and we have only succeeded in isolating in a pure state for analysis small samples of the monoethyl tri-iodide and the triethyl monobromide. Thus when the ethyl base was mixed with half an equivalent of hydrogen iodide, triethyltelluronium iodide was obtained as a sparingly soluble, pale yellow product, m. p. 115° (Found: I, 35.7. Calc.: I, 37.2%), but we did not succeed in separating the salt in a pure state. With hydrogen bromide, however, a *colourless* soluble salt was obtained, which decomposed at 215° and was identified as triethyltelluronium bromide (Found: Br, 26.9. Calc. for C₆H₁₅BrTe: Br, 27.2%). The residue, which should contain telluropropionic acid, gave with hydrogen bromide a yellow oil, which was perhaps ethyltelluronium

tribromide; but since this was not obtained in sufficient quantities for adequate purification, involving in this case a separation from the liquid " β -dibromide," it was not analysed.

More successful results were obtained by working with a solution of the solid " β -di-iodide" in acetone. Thus, when this solution was mixed with a solution of potassium iodide in acetone, a colourless precipitate was obtained, which had the general properties of triethyltelluronium iodide, since it was readily soluble in water and gave a neutral solution from which no precipitate was thrown down by the addition of aqueous hydrogen iodide. On the other hand, when a solution in acetone of the crude " β -di-iodide" (obtained by adding hydrogen iodide to a solution of the " α -tellurone" in dilute hydrochloric acid) was merely diluted with chloroform, the solution slowly deposited black needles, decomposing at 135° , which were identified as the hitherto-unknown *ethyltelluronium tri-iodide* (Found: I, 71.0. $C_2H_5TeI_3$ requires I, 70.7%). This compound gave a colourless solution in water, which had a strongly acid reaction and was evidently hydrolysed extensively like the trimethyl compound.

Synthetic experiments in the diethyl series are only practicable in the case of the " β -di-iodide," since the dichlorides and dibromides are liquid, and they are rendered difficult by the ease with which the complex salts of this series are dissociated. Thus, whereas the trimethyl iodide dissolves in acetone in presence of the methyl tri-iodide to form the double salt $(TeMe_3)TeMeI_4$, pure acetone and pure methyl alcohol merely extract the soluble monoethyl tri-iodide from a mixture with powdered triethyl monoiodide, and deposit it in an impure form, instead of giving the double salt. Similar results were obtained when an attempt was made to prepare a mixed double salt from the triethyl monobromide and the monoethyl tri-iodide. Up to the present, therefore, we have only been able to establish the structure of these β -salts by analysis and not by synthesis.

6. Structure of the Tellurones.

The experiments described below were made in order to test, in the light of Drew's experiments, the earlier statements of Vernon, who prepared dimethyltellurone, $TeMe_2O_2$ (C, 10.50; H, 3.19. Calc.: C, 12.6; H, 3.20%), by evaporating an aqueous solution of the α -base with hydrogen peroxide, and described it as an insoluble amorphous powder, which decolorised permanganate and liberated halogens from the halogen acids. He then stated, but without giving any experimental details, (i) that "the tellurone gives β -dihaloids with halogen acids," (ii) that the β -base gave the same product, although it was oxidised less readily than the α -base.

Our experiments have confirmed the first of these two statements, since we have obtained good yields of pure " β -di-iodide" by oxidising Vernon's α -base to the tellurone, dissolving the insoluble tellurone in very dilute hydrochloric acid, and then adding a more concentrated solution of hydriodic acid or of potassium iodide to precipitate the insoluble " β -di-iodide." Good yields of the " β -di-iodide" have also been obtained in the diethyl series by recrystallising from methyl alcohol (instead of from acetone by the addition of chloroform) the crude product obtained by the action of hydriodic acid on the insoluble tellurone (Found: Te, 58.0. Calc.: Te, 58.6%) formed by atmospheric oxidation of the α -base. These observations are important, since they prove that the Vernon transformation can be effected, not only by desiccating the α -base, but even more readily by oxidising the α -base to a tellurone and then reducing this to a β -salt by the action of a halogen acid; they show, moreover, that this type of transformation can be effected by either process in the corresponding compounds of the ethyl series.

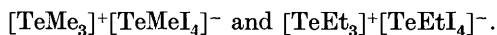
Unexpected difficulties were encountered, however, in attempting to confirm the second of Vernon's statements, since we have not found it possible to prepare a typical specimen of the tellurone by the action of hydrogen peroxide on the β -base of either series. Thus, whereas the oxidation product from Vernon's α -base was insoluble in water (but soluble in dilute hydrochloric acid, of which it reduced the conductivity very considerably), the oxidation product from the β -base was a soluble deliquescent salt with a high conductivity of its own ($\Lambda = 112$ — 131 at $v = 98$ — 784 , for two atoms of tellurium). In the same way the oxidation of the β -base of the diethyl series gave a soluble deliquescent product, which gave $\Lambda = 176$ — 231 at $v = 135$ — 1080 , also calculated on two atoms of tellurium.

A clue to the origin of these differences was obtained by oxidising Vernon's β -base with hydrogen peroxide and reducing the product with hydrogen iodide, whereby an insoluble black residue of " β -di-iodide" was obtained, together with a dark red solution from which Drew's monomethyltelluronium tri-iodide, TeMeI_3 , could be extracted with ether. If we regard the β -base as a mixture of TeMe_3OH and $\text{Me}\cdot\text{TeO}\cdot\text{OH}$, these observations show clearly that there has been a preferential oxidation of the trimethyltelluronium radical, since the monomethyl radical is now in excess. The loss of carbon from the system was also confirmed by analysis, since the soluble deliquescent product, for which conductivity data are cited above, gave C, 8.64; H, 2.28; whereas the calculated values are: for TeMe_2O_2 , C, 12.6; H, 3.16; for TeMe_2O , C, 12.03; H, 3.01; for $\text{TeMeO}\cdot\text{OH}$, C, 6.9; H, 2.29; and for its anhydride, C, 7.2; H, 1.8%. The percentage of carbon is even lower than that

found by Vernon, but the analysis corresponds fairly well with the composition deduced for a sample of β -base which had been oxidised partially to telluracetic acid.

A similar destruction of the trimethyl radical was observed when Vernon's α -base was oxidised to the tellurone and then acted upon by hydrobromic acid. Instead of the insoluble β -dibromide, a yellow solution was obtained, from which Drew's monomethyl-telluronium tribromide could be extracted with ether; the trimethyl monobromide had presumably been oxidised away by the bromine set free from the acid by the oxygen of the tellurone. Preferential oxidation of the trialkyl radical appears to take place even more easily in the ethyl series, where a soluble deliquescent product was obtained by oxidising the α -base with hydrogen peroxide and evaporating the solution to dryness, although a typical insoluble tellurone was obtained from the base by atmospheric oxidation.

In view of these results, we concur with Drew in the conclusion that Vernon's oxidation product was not a tellurone, since we regard it as unlikely that a methyl or ethyl radical should migrate during the conversion of our oxidation products into β -salts under the conditions described above. On the other hand, if the trimethyl- or triethyl-telluronium radical was already present in these oxidation products, Vernon's analyses and our own justify us in formulating them as $[\text{TeMe}_3]^+[\text{TeMeO}_4]^-$ and $[\text{TeEt}_3]^+[\text{TeEtO}_4]^-$, their sparing solubility corresponding with that of the " β -dihalides,"



The soluble oxidation products from the β -bases are perhaps mixtures of the unchanged base with free telluracetic or telluropropionic acid.

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