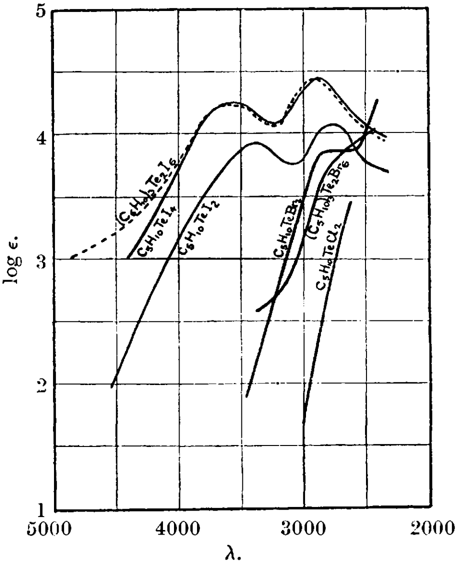
CCCL.—*Studies in Valency. Part XI. Molecular Conductivities and Extinction Coefficients of Derivatives of* cyclo*Telluropentane.*

By Frank Lathe Gilbert and Thomas Martin Lowry.

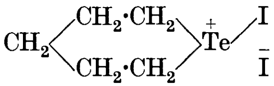
Through the kindness of Professor G. T. Morgan and Dr. H. Burgess, we have been able to extend our investigation of the dimethyltelluronium salts (this vol., pp. 307, 1997) by measuring the molecular extinction coefficients in dry alcohol, and the molecular conductivities in water, of the compounds of *cyclo*telluropentane recently described by them (*ibid.*, p. 321). In addition to examining the dihalides of the three series, represented by (I), (II), and (III), we have prepared and examined the base $C_5H_{10}TeO$ or $C_5H_{10}Te(OH)_2$, the hydroxy-halides $C_5H_{10}Te(OH)X$, and the *tetraiodide* $C_5H_{10}TeI_4$, of the monocyclic series, and the base $(C_5H_{10})_3Te_2(OH)_2$ of the dicyclic series, as well as the bistribromide and the *bistri-iodide* of the latter series. In the case of the bases, the measurements included a potentiometric titration.

Fig. 1.

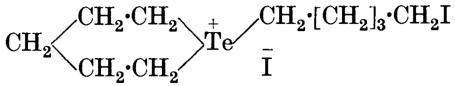
Molecular extinction coefficients of cyclic tellurium compounds.



Absorption Spectra.—The molecular extinction coefficients are plotted in Fig. 1 and the most important values are summarised in Table I. Most of the observations followed the course that we should have anticipated on the assumption that the dihalides may be represented by formulæ such as (I), (II), and (III), where the

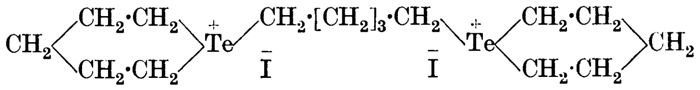


(I.)



(II.)

(III.)



covalent and electrovalent halogen are distinguished in the usual way. Thus the cyclic dichloride gave only a general absorption, as in the case of the two dimethyl compounds. The cyclic dibromide, however, gave a step-out, log $\varepsilon = 3{\cdot}85$ at λ 2600—2850, just as in the case of the α- and β-dimethyl compounds, which gave a similar step-out, log $\varepsilon = 3{\cdot}7$ and 4·0, respectively, at λ 2600—2800. At longer wave-lengths, however, the absorption of the cyclic dibromide agrees closely with that of the α-dibromide, and is very much less than that of the β-dibromide, which is sufficiently strong in the visible region to give the compound a bright yellow colour, which is lacking both in the isomeric α-compound and in the cyclic dibromide.

The monocyclic di-iodide (I) separates from hot or cold benzene in a purple form, but the surface becomes yellow if the solution is allowed to dry on the crystals. When the purple form is heated, it begins to pass into the orange form at about 90° and changes rapidly at 110°; the purple form also becomes orange in boiling water before it dissolves. The transition temperature is therefore below 100°, but is not easy to determine precisely on account of the lag in the transformation, even with rising temperatures. The reverse change from orange to purple takes place in a few minutes at the ordinary temperature, but is slower if the orange form has been kept for some time above 100°. The clear orange crystals which are obtained when the di-iodide separates from hot carbon tetrachloride may persist for some weeks at atmospheric temperature before becoming purple, even when exposed to air and light; and a crystal which exhibits both colours may persist for some days before it changes completely into the purple form.

A careful comparison showed that the absorption spectra of the two forms in cold alcoholic solutions are identical within the limits of experimental error. The spectrum shows the twin maxima of the " iodoform band," the maximum extinction coefficients being log $\varepsilon = 3{\cdot}9$ at 3380 and log $\varepsilon = 4{\cdot}05$ at 2770. The intensities of two maxima are similar to those of the dimethyl di-iodides (of which the α-compound gave log ε = 3·7 and 4·05, whilst the β-compound gave log ε = 3·8 and 4·25), but in the visible region the absorption of the cyclic di-iodide again corresponds with that of the α-dimethyl di-iodide, since the curve falls away steeply from the maximum, instead of showing the wide extension of the foot of the band which accounts for the deeper colour of the β-di-iodide.

The cyclic di-iodide (I) also resembles the α-dimethyl di-iodide, and differs from the β-di-iodide in that it readily forms a tetraiodide $[C_5H_{10}TeI]^+I_3^-$. This compound, which we prepared by mixing equimolecular solutions of the di-iodide and of iodine in chloroform, and boiling the mixture under reflux for 10 minutes, separated as a black solid, and crystallised from methyl alcohol in shining, black crystals. It melts at 82—84° to a black oil, which is slowly dissolved (like the di-iodide) by boiling water, but to a very limited extent. Its absorption spectrum is similar to that of the di-iodide, but of practically twice the intensity throughout, since both ions of the salt give rise to twin maxima at nearly the same wave-length and intensity (log ε = 4·28 and 4·45, obs.; 4·25 and 4·43, calc.).

According to the views expressed in our previous paper, *both* atoms of halogen in the dihalides of type (III) should be ionised in the same way as in the trimethyltelluronium halides. This conclusion is confirmed by the fact that the di-iodide $(C_5H_{10})_3Te_2I_2$ is readily converted into a black hexaiodide, $(C_5H_{10})_3Te_2I_6$. This compound, which we prepared by mixing the cyclic di-iodide with 2 mols. of iodine in chloroform, and boiling the mixture under reflux for 10 minutes, separated as a black solid melting at 127—129°, but could not be recrystallised on account of its sparing solubility. In order to observe its absorption spectrum, 0·0125 g. was dissolved in 10 c.c. of dry methyl alcohol, and the solution examined at *M*/5000. The spectrum showed the twin maxima of the tri-iodide ion, with the same two-fold intensity as in the monocyclic tetraiodide (log ε = 4·25 and 4·44, obs.; 4·30 and 4·50, calc.), but with a wider " foot " in the visible region of the spectrum, to correspond with the greater absorption in this region of the tri-iodide ions. The hexabromide, described by Morgan, was also examined in methyl alcohol, and gave a general absorption with clear indications of a maximum, log ε >4, just beyond λ 2400, and the beginnings of a step-out, which could not be traced to longer wave-lengths than 3400 on account of the limited solubility of the product (the tribromide ion in $C_6H_4Br\cdot\overset{+}{N}Me_3\overset{-}{Br_3}$ gives a maximum, log ε = 3·4 at λ 2600, and a step-out, log ε = 1·8 at λ 3900).

The remaining compounds of series (II) and (III) gave only a general absorption of light, in agreement with the conclusion that

TABLE I.

Extinction Coefficients in Alcohol of Halogen Derivatives of cyclo-*Telluropentane.*

(*a*) Selective absorption.

		λ.	log ε.	λ.	log ε.
$C_5H_{10}TeI_2$	Maxima at	3380	3·92	2770	4·05
$C_5H_{10}TeI_4$	,, ,,	3560	4·28	2880	4·45
$(C_5H_{10})_3Te_2I_6$ (in MeOH)	,, ,,	3560	4·26	2900	4·44
$C_5H_{10}TeBr_2$	Step-out at λ = 2600 to 2850.			log ε = 3·85.	

(*b*) General absorption.

	Wave-lengths for integral values of log ε.					
	log ε = 1·5.	2·0.	2·5.	3·0.	3·5.	4·0.
$C_5H_{10}TeCl_2$		2950	2840	2730		
$C_5H_{10}Te(OH)I$ (in water)		2870	2690	2480		
$(C_5H_{10})_2TeI_2$	3460	3130	2980	2750		
$(C_5H_{10})_2TeBr_2$		2800	2500	2340		
$(C_5H_{10})_2TeCl_2$	2680	2520	2340			
$(C_5H_{10})_3Te_2Br_2$		2900	2580	2420		
$(C_5H_{10})_3Te_2I_2$				2830	2330	
$(C_5H_{10})_3Te_2Br_6$ (in MeOH)				3070	2920	2500

none of the halogen is joined to the metal by a covalent bond. The rather heavy general absorption of the iodide (II) can be explained by the presence of the group $-CH_2I$, but this explanation is not available in the case of the iodide (III).

Molecular Conductivities.—The methods used have already been described (this vol., p. 308), but attention may be directed to the fact that a few sparingly soluble compounds, which it was undesirable to hydrolyse by boiling with water, were dissolved in a minimum quantity of alcohol and diluted with not less than 20 volumes of conductivity water. The validity of the corrections applied to these solutions has already been demonstrated in the case of α-dimethyltelluronium di-iodide (this vol., p. 313).

The molecular conductivities shown in Table II are for the most part in agreement with the values which we should have predicted from the preceding formulæ, with the help of the data already obtained for the dimethyl compounds. Thus, the dihalides of type (II) behave as *binary* electrolytes, like the hydroxy-halides of the dimethyl series, or the simple halides of the trimethyl series, and give values of Λ^{25° = *ca.* 100. In the same way, the dihalides of type (III) behave as *ternary* electrolytes, giving Λ^{25° = *ca.* 200. The dihalides of type (I), however, gave the same anomalous values, Λ^{25° = *ca.* 500, which were observed previously in the dimethyl series, so that once more it was clear that, whereas one halogen is *ionised* more or less completely, the other is *hydrolysed* to a similar degree. The tetraiodide of type (I) gave similar values, Λ^{25° = *ca.* 500, and was evidently hydrolysed according to the scheme

$$[C_5H_{10}TeI]I_3 + H_2O \rightleftharpoons [C_5H_{10}TeOH]I_3 + HI.$$

An unexpected result was obtained, however, when the bis-tribromide of type (III) and the analogous bis-tri-iodide were dissolved in boiling water and cooled to 25°, since, instead of behaving as ternary electrolytes, with $\Lambda^{25^\circ} = ca.\ 200$, their solutions gave molecular conductivities of the order $\Lambda^{25^\circ} = 1000$. This anomaly can be explained most readily by supposing that the compounds are decomposed according to the scheme

$$C_5H_{10}:TeI_3\cdot C_5H_{10}\cdot TeI_3:C_5H_{10} \longrightarrow 2C_5H_{10}:TeI_2 + C_5H_{10}I_2$$
$$\longrightarrow 2[C_5H_{10}:TeOH]I + 2HI + C_5H_{10}I_2$$

The conclusion that the high conductivities of this compound are due to a progressive decomposition was established by dissolving the polyiodide in cold alcohol and diluting it with cold water, whereupon we found $\Lambda^{25^\circ} = 106$, reckoned on the total concentration of the polyiodide, part of which, however, was still undissolved. When the solution was warmed, the value rose to $\Lambda = 136$ at 40°, and $\Lambda = 315$ at 100°. Finally, after some minutes' boiling, when all the material had dissolved, the conductivity rose to $\Lambda^{25^\circ} = 794$, or $\Lambda^{25^\circ} = 930$ when corrected for the alcohol used as solvent, in good general agreement with the values recorded in Table I.

The hydroxy-halides, which are formed by the hydrolysis of the monocyclic dihalides, were prepared by mixing the free base (see below) and the dihalides in molecular proportions, and were found to behave as strong binary electrolytes, just as in the case of the hydroxy-halides prepared from Vernon's salts. The conductivities agree more nearly with those of the α-series than of the β-series, but we cannot lay any stress on this fact, as we have not yet found a satisfactory explanation of the higher values recorded for the latter compounds. In the case of the free bases, however, where there is a much greater contrast between the α- and β-series, the conductivities of the cyclic compound are much lower than those of Vernon's β-base, and differ only to an insignificant extent from the very small values already recorded for the α-base at similar dilutions.

Potentiometric Titration of the Bases.—(*a*) The *monocyclic base*, $C_5H_{10}Te(OH)_2$ or $C_5H_{10}TeO$, was prepared by grinding the dibromide with freshly prepared silver oxide; when the solution was evaporated to dryness in a vacuum, the base was obtained as a colourless solid, but the quantity was not sufficient for an analysis to show whether the base was anhydrous or hydrated. On re-dissolving, it gave the same reactions as the original base with acids, with silver nitrate, and with ferric chloride, and hence was not converted into an isomeride under the conditions which cause Vernon's α-base to change into the β-base. With hydriodic acid, the base gives a

TABLE II.

Molecular Conductivities Λ^{25° *of Derivatives of* cyclo*Telluropentane.*

	v = 128.	256.	512.	1024.	2048.	4096.
Type I.						
$C_5H_{10}TeCl_2$		475	482	491	482	478
$C_5H_{10}TeBr_2$		481	485	493	492	489
$C_5H_{10}TeI_2$ (orange)			476	484	484	469
$C_5H_{10}TeI_2$ (purple)			473	486	493	478
$C_5H_{10}TeI_2$ (purple) 5% alcohol at v = 512 (corrected values).			474	479	483	474
$C_5H_{10}TeI_4$ 4·5% alcohol at v = 1024 (corrected values).				488	491	493
$C_5H_{10}Te(OH)Cl$	96	98	102	105	107	112
$C_5H_{10}Te(OH)Br$	96	100	104	108	110	112
$C_5H_{10}Te(OH)I$		97	102	107	110	111
$C_5H_{10}Te(OH)_2$	5·5*	6·4	8·0	10·6		
Type II.						
$(C_5H_{10})_2TeCl_2$		92·5	94·4	96·5	98	101
$(C_5H_{10})_2TeBr_2$		90·5	94·4	96·5	99	102
$(C_5H_{10})_2TeI_2$		92	96	98	101·5	104
Type III.						
$(C_5H_{10})_3Te_2Br_2$		199	209	219	225	232
$(C_5H_{10})_3Te_2I_2$		185	197	206	213	219
$(C_5H_{10})_3Te_2Br_6$			1074	1098	1115	1114
$(C_5H_{10})_3Te_2I_6$					965†	986‡

* At v = 42·6, Λ^{25° = 4·2, and at v = 64, Λ^{25° = 4·6.

† For v = 2260. ‡ For v = 4520.

canary-yellow precipitate, m. p. 136—137°, which is probably the orange form of the cyclic di-iodide, m. p. 135—136°. This precipitate does not change colour when heated to its m. p., but turns purple (or dark red) when compressed with a spatula, and retains this colour when the pressure is released. The dark red form reverts to the yellow form at 115°, but this does not change back to red on cooling.

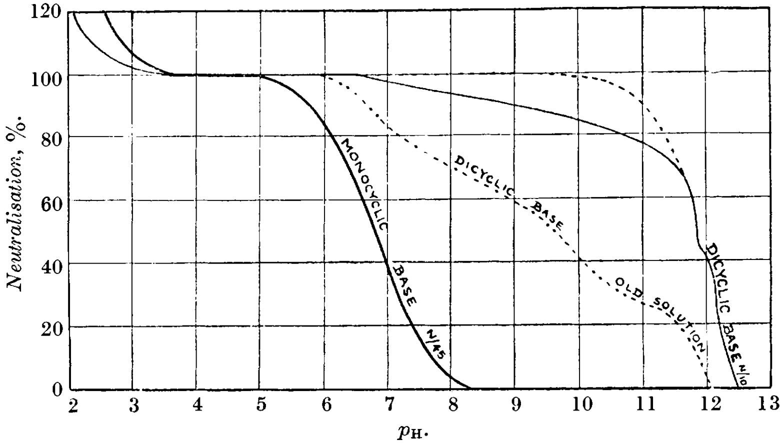
A potentiometric titration was made, with a glass electrode, of an $N/45$-solution, which was neutralised with N-hydrochloric acid. The resulting curve is plotted in Fig. 2. The free base gave $p_H = 8{\cdot}3$, in close agreement with the value for the α-dimethyl base. The equivalence point was $p_H = 4{\cdot}1$, the values at 98% and 102% neutralisation being 5·1 and 3·4, a range of 1·7 units. At half-neutralisation $p_H = 6{\cdot}8$, whence $-\log K_B = 7{\cdot}2$ and $K_B = 6{\cdot}3 \times 10^{-8}$. The titration curve almost coincides with that of Vernon's α-base; but it differs fundamentally from the curve for the β-base, in that it shows no sign of an intermediate inflexion.

(*b*) The *dicyclic base*, $(C_5H_{10})_3Te_2(OH)_2$, was prepared by the action of silver oxide on the di-iodide or dibromide. In order to obtain a good yield, it was necessary to grind the di-iodide with silver oxide for 2—3 hours, whereas $\frac{1}{2}$ hour is ample for the conversion of the monocyclic di-iodide and the dimethyl di-iodides into the corresponding bases. A quantitative experiment with a weighed quantity of the dicyclic di-iodide showed that under these conditions the neutral point with methyl-orange corresponds closely with that calculated for neutralisation of both hydroxyl groups of the base. After evaporation and dissolution, the base gave the same reactions as before towards silver nitrate, picric acid, hydriodic acid, and ferric chloride.

A curve for the potentiometric titration of an $N/10$-solution of the dicyclic base with a glass electrode against N-hydrochloric acid

FIG. 2.

Potentiometric titrations.



is shown in Fig. 2. The solution was freshly prepared, since less than 1 hour elapsed between the preparation of the base and the commencement of the titration. The dicyclic compound is a strong base, which gave $p_{\mathrm{H}} = 12{\cdot}5$ at $N/10$ or $M/20$, in marked contrast with the weak monocyclic base, which gave $p_{\mathrm{H}} = 8{\cdot}3$ at $N/45$. A slight break, corresponding to the neutralisation of the first hydroxyl group, was observed at 50% neutralisation, but this could easily have been obliterated in drawing the diagram. At about 75% neutralisation the readings became unstable and began to drift towards the alkaline side, the largest drift being about 44 millivolts or 0·8 in the value of p_{H}. The values plotted in Fig. 2 were obtained after an interval of about 15 minutes, when the drift had become very slow; but we cannot be sure that they were the final equilibrium values, and it is possible that after long delay the values might have drifted to those required to give the typical (broken) curve for a strong base. At 80—100% neutralisation the drift was more rapid, and at 100% steady values were obtained immediately.

The abnormalities described above were confirmed in almost every detail by a duplicate determination with a freshly prepared $N/14{\cdot}5$ (or $M/29$)-solution. A third solution, of concentration $N/14$, which had been made up for about 9 days, however, gave a more abnormal curve, which straggled across from an initial value $p_{\mathrm{H}} = 12$, to $p_{\mathrm{H}} = 6$ at 100% neutralisation. Similar abnormalities were observed in the conductivities of these solutions. Thus the equivalent conductivities of the solution which was used for the first potentiometric titration, when examined 2 days after it had been prepared, had the following values at 20° :

v	71·5	143	286	572	1144
$\Lambda^{20°}$	190	195	197	197	196

Since the mobility of the bivalent kation $(C_5H_{10})_3Te_2^{++}$ is about 34×2, whilst that of the hydroxyl ion at 20° is about 178, these are normal values for a strong base with $\Lambda_{\infty}^{20°} = ca.\ 210$. On the other hand, the third solution, when 10 days old, gave the following equivalent conductivities at 25° :

v	100	200	400	800	1600
$\Lambda^{25°}$	116	122	126	129	129

These conductivities are about one-third less than those recorded for the first solution, whereas they should be about 8 units higher to allow for a temperature difference of 5°.

Although we cannot offer any precise explanation of these anomalies, they are clearly due to a locking-up of the basic properties of the hydroxide by a reversible process which may be compared with the formation of a pseudo-base. This view is supported by the fact that a progressive decrease of conductivity was observed in a freshly prepared solution of the base, which gave the following readings (R = resistance ; t = time, in hours) :

t ...	0	0·5	1	2·8	4·5	6	22	46	95	101	119	142
R ...	88·5	90·1	90·8	90·9	91·1	91·3	93·8	96·8	101·5	102	103·5	105
$\Lambda_{59}^{25°}$	142										121·5	119·5

In this case, the conductivity fell progressively from an initial value, which was approximately mid-way between those of the first and third solutions, to a final value, which was approximately the same as the latter. The strength of the solution, as tested by titration with methyl-orange as indicator, however, was exactly the same at the end of 6 days as when tested initially. On the other hand, another freshly prepared solution had already reached a steady value $\Lambda_{47}^{25°} = 117$ at the end of 5 minutes from the time when the base was extracted from the silver oxide, and maintained it with small fluctuations during a period of 2 days :

t	0·1	0·4	2·5	4	5·5	21·5	30	46	48
R	86·0	86·0	85·4	85·0	85·6	85·2	87·5	87·0	87·0

These observations show that solutions of the dicyclic base are subject to wide variations of properties, depending on the age of the solutions and on other factors which are still obscure; but no more material was available to enable us to pursue the enquiry any further.

Action of Alkalis on the Cyclic Di-iodide.—The most striking contrast between Vernon's α- and β-compounds is found in the fact that the α-di-iodide yields sparingly soluble basic iodides when acted on by alkalis, whilst the β-di-iodide undergoes a molecular rearrangement, which can be compared with a pinacol–pinacolin transformation, since it gives rise to trimethyltelluronium iodide as one of the products. In order to find out which type of behaviour is characteristic of the monocyclic iodides, the purple di-iodide was boiled with a concentrated aqueous solution of potassium carbonate, and evaporated to a small bulk. The colourless crystals which separated decomposed at 195° and contained 39—41% I, whereas the monoxyiodide $(C_5H_{10})_2Te_2OI_2$ would require 38·3% I. The compound resembled Vernon's α-monoxyiodide in being soluble in water and neutral to methyl-orange, but differed from it in that it did not change colour in air.

A colourless solid obtained by grinding the solid di-iodide with concentrated aqueous ammonia turned yellow on exposure to the air or when heated at 100°; it contained 34% of iodine, gave a neutral aqueous solution, and blackened and decomposed at 150°.

The products obtained by the action of potassium carbonate and of ammonia on the monocyclic di-iodide are obviously quite distinct from the dicyclic di-iodide, $(C_5H_{10})_3Te_2I_2$, which would be the analogue of the trimethyltelluronium iodide formed in Vernon's transformation of the β-salt; on the other hand, their composition and properties are those of basic iodides, and therefore confirm the conclusion that in this respect also the cyclic di-iodide exhibits the behaviour of an α- rather than of a β-salt.

Summary.

Measurements have been made of the molecular conductivities and extinction coefficients of the cyclic tellurium compounds recently described by Morgan and Burgess. The tertiary salts behave as strong electrolytes, like $TeMe_3I$, but the secondary salts resemble $TeMe_2I_2$ in losing one molecule of halogen by hydrolysis,

giving rise to hydroxy-halides. Observations of the conductivities of the base and of the form of the curve obtained from a potentiometric titration, together with the absorption spectrum of the iodide and its behaviour towards iodine and towards alkalis, show that the cyclic compounds resemble Vernon's α- (or *trans*-) series of compounds rather than the isomeric β- (or *cis*-) compounds.

We are indebted to Professor Morgan and Dr. Burgess for specimens of the cyclic tellurium compounds, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (F. L. G.) during the period within which the research now described was carried out.

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