935. *The Conductances of Some Chlorides in Ethanol. Part II.*[1] *Electrolytic Behaviour of Zirconium Chloride Ethoxides.*

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The conductances of zirconium chloride ethoxides, $ZrCl_n(OEt)_{4-n}$, where $n = 3$, 2, or 1, have been measured in very dilute solution in ethanol at 25° over a range of concentrations. The limiting molar conductances and the variation of conductance with concentration suggest in each case the presence of solvolytic equilibria involving the formation of hydrochloric acid. However, it does not seem possible to determine the precise nature of these equilibria from conductance data alone.

Recently [1] we studied the electrolytic behaviour of alcoholic solutions of hydrochloric acid, cæsium chloride, magnesium chloride, and lanthanum chloride in order to obtain information to interpret the electrolytic behaviour of Group IV metal chlorides. Now we report the conductances of three zirconium chloride ethoxides. Zirconium tetrachloride reacts with ethyl alcohol [2] and was not included in this study.

The aqueous solution chemistry of zirconium is complicated by hydrolysis and hydrolytic polymerisation and it seemed reasonable to expect a much simpler situation in solutions of chloride ethoxides in ethyl alcohol. Moreover, the results were expected to throw some light on the problem of the mechanism of formation of zirconium tetraalkoxides.

Experimental

*Zirconium Monochloride Tri*iso*propoxide.*—Zirconium *iso*propoxide solvate (18·7 g.) in benzene (100 c.c.) was treated with acetyl chloride (3·8 g.). After boiling for 2 hr. the solution was evaporated to dryness under reduced pressure and the monochloride tri*iso*propoxide *solvate* (10 g.) obtained after two recrystallisations from benzene [Found: Zr, 25·4; Cl, 9·8; Pr^iO, 64·7. $ZrCl(OPr^i)_3,Pr^iOH$ requires Zr, 25·1; Cl, 9·7; Pr^iO, 64·9%].

*Zirconium Dichloride Di*iso*propoxide.*—Zirconium *iso*propoxide solvate (7·2 g.) was caused to react with acetyl chloride (2·9 g.) in benzene (100 c.c.), and the solid product isolated as before. The dichloride di*iso*propoxide *solvate* was purified by three recrystallisations from carbon tetrachloride [Found: Zr, 26·9; Cl, 20·7; Pr^iO, 52·1. $ZrCl_2(OPr^i)_2,Pr^iOH$ requires Zr, 26·8; Cl, 20·8; Pr^iO, 52·1%].

Zirconium Trichloride Monoethoxide.—Zirconium tetrachloride (17·9 g.) suspended in benzene (250 c.c.) was treated with a mixture of ethyl alcohol (7·05 g.) and benzene (100 c.c.). After boiling for 1½ hr. the solution was filtered and the filtrate evaporated to dryness under reduced pressure. The pure trichloride monoethoxide *solvate* was obtained after four

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[1] Part I, Aggan, Bradley, and Wardlaw, *J.*, 1958, 2092.

[2] Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

recrystallisations from benzene [Found: Zr, 31·7; Cl, 36·7; EtO, 31·1. $ZrCl_3(OEt),EtOH$ requires Zr, 31·6; Cl, 36·8; EtO, 31·2%].

Measurement of Conductances in Ethyl Alcohol.—The methods of preparation of "conductivity" alcohol, of solutions of the zirconium chloride alkoxides in the alcohol, and the apparatus used for the measurement of conductances have been described.[1] All measurements were at 25°.

RESULTS AND DISCUSSION

Zirconium Monochloride Triisopropoxide.—The conductances were measured at several concentrations in the range 10^{-5}—$1·5 \times 10^{-4}$M and did not change with time. Although the monochloride tri*iso*propoxide was used because it can be purified more readily than the monochloride triethoxide, alcohol interchange ensures that it is the behaviour of the monochloride triethoxide which is studied. The results are given in Table 1 where Λ_m is the molar conductance and C_m the concentration in moles/litre. A plot of $\Lambda_m C_m$ against $1/\Lambda_m$ showed that the simple Ostwald equation was obeyed and $\Lambda_{calc.}$ (in Table 1) is the value calculated from this with the apparent limiting conductance $\Lambda_0' = 72·31$ and $K' = 1·087 \times 10^{-4}$.

TABLE 1.

$10^5 C_m$	Λ_m	$\Lambda_{calc.}$	$10^5 K$	$10^5 C_m$	Λ_m	$\Lambda_{calc.}$	$10^5 K$
1·165	65·99	65·88	9·42	6·165	51·47	51·50	9·86
2·067	62·18	62·11	9·75	7·029	49·92	49·97	9·82
2·530	60·63	60·50	9·87	8·262	47·86	48·03	9·69
3·062	58·72	58·83	9·70	9·651	46·16	46·15	9·84
3·630	57·13	57·20	9·78	11·314	44·12	44·19	9·75
4·345	55·34	55·38	9·85	13·227	42·23	42·26	9·76
5·261	53·28	53·27	9·85	15·280	40·51	40·47	9·78

The excellent agreement between Λ_m and $\Lambda_{calc.}$ is reflected in the percentage standard deviation of ±0·15%. To allow for interionic effects the results were treated by Fuoss's method[3] with use of the simple expression for the mean activity coefficient: $-\log f_{\pm}^2 = 5·954\sqrt{(\alpha C_m)}$, where α is the degree of ionisation. This gave the limiting equivalent conductance $\Lambda_0 = 73·65$ and the thermodynamic dissociation constant $K = 9·78 \times 10^{-5}$. Values for K given in Table 1 were computed for each experimental point. This procedure is very sensitive to experimental error but the percentage standard deviation of ±0·9% for K and the distribution of sign in the deviations leaves no doubt that the zirconium monochloride triethoxide behaves as a weak uni-univalent electroyte in ethyl alcohol. Zirconium tetra*iso*propoxide behaves as a non-electrolyte in ethyl alcohol, so part of the conductance of zirconium monochloride triethoxide must be attributed to ionisation of the chlorine. However, the limiting conductance is very high for a univalent chloride, being near to that (82·46 [1]) for hydrochloric acid. Therefore, a simple ionisation of the type

$$ZrCl(OEt)_3 \rightleftharpoons Zr(OEt)_3^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

seems improbable because this would require a Λ_0 of *ca.* 50 (cf. CsCl 48·01 [1]). Solvolysis seems indicated, *i.e.*,

$$ZrCl(OEt)_3 + EtOH \rightleftharpoons Zr(OEt)_4 + H^+ + Cl^- \quad . \quad . \quad . \quad . \quad (2)$$

This would require a linear relation between $(\Lambda_m C_m)^2$ and $1/\Lambda_m$, which is not found. The simultaneous operation of mechanisms (1) and (2) would cause $\Lambda_m C_m$ to be independent of C_m which is also contrary to our results. A fourth possibility is complete ionisation in (1) with simultaneous reversible solvation as in (3):

$$Zr(OEt)_3^+ + EtOH \rightleftharpoons Zr(OEt)_4 + H^+ \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[3] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

This would require the following relation between Λ_m and C_m:

$$\{K_3[\lambda^\circ_{H^+} - \lambda^\circ_{Zr(OEt)_3^+}](\Lambda^\circ_{HCl} - \Lambda_m)\}^{\frac{1}{2}}/C_m^{\frac{1}{2}} = \Lambda_m - [\lambda^\circ_{Zr(OEt)_3^+} + \lambda^\circ_{Cl^-}] \quad . \quad (4)$$

Thus a plot of $(\Lambda^\circ_{HCl} - \Lambda_m)^{\frac{1}{2}}/C_m^{\frac{1}{2}}$ against Λ_m should be linear but this was not the case when $\Lambda^\circ_{HCl} = 82{\cdot}46$ was used. A straight line resulted from $\Lambda^\circ_{HCl} = 73{\cdot}65$ but the values of the term in the last bracket of eqn. (4) then obtained by substitution in eqn. (4) were impossibly low. Finally, in view of the proximity of Λ_0 to the value for hydrochloric acid we considered the possibility of complete solvolysis, *i.e.*,

$$ZrCl(OEt)_3 + EtOH \longrightarrow Zr(OEt)_4 + H^+ + Cl^- \quad . \quad . \quad . \quad . \quad (5)$$

The solution of zirconium monochloride triethoxide would then behave electrolytically like hydrochloric acid of the same molar concentration. Unfortunately this also is not the case because we have previously shown [1] for hydrochloric acid that $K = 8{\cdot}23 \times 10^{-3}$ whereas the data in Table 1 show clearly that $K = 9{\cdot}78 \times 10^{-5}$. The only remaining possibility is that the monochloride ionises according to equation (1) but that the solvated ion $Zr(OEt)_3^+$ has an anomalously high mobility due to some special mechanism of conduction.

*Zirconium Dichloride Di*iso*propoxide.*—The molar conductances for the dichloride over the concentration range 5—50 × 10^{-5} molar gave a convincing Ostwald plot as shown by the agreement between Λ_m and $\Lambda_{calc.}$ in Table 2. Values of $\Lambda_{calc.}$ were computed by use of the apparent limiting molar conductance $\Lambda_0' = 144{\cdot}1$ and $K' = 6{\cdot}644 \times 10^{-5}$ and the percentage standard deviation was $\pm 0{\cdot}37\%$.

TABLE 2.

10^5C_m	Λ_m	$\Lambda_{calc.}$	10^5K	10^5C_m	Λ_m	$\Lambda_{calc.}$	10^5K
4·756	97·07	97·11	9·79	11·79	75·12	74·90	10·16
5·609	92·56	93·20	9·65	14·18	70·51	70·51	10·09
6·584	89·28	89·28	9·97	16·88	66·24	66·39	10·02
7·737	85·76	85·25	10·19	22·02	60·35	60·33	10·06
8·899	81·82	81·80	10·04	50·45	43·58	43·66	9·81
10·10	79·09	78·69	10·21				

The high value of Λ_0' [almost twice that for $ZrCl(OEt)_3$] again suggested the formation of hydrochloric acid and we explored the possibility of complete solvolysis:

$$ZrCl_2(OEt)_2 + 2EtOH \longrightarrow Zr(OEt)_4 + 2H^+ + 2Cl^- . \quad . \quad . \quad . \quad (6)$$

Fuoss's method [3] was applied to the data in the form of *equivalent* conductances and normalities (based on eqn. 6). Activities were calculated as for the monochloride and the appropriate functions of Fuoss's treatment gave the required linear relationship. The limiting *equivalent* conductance was 77·15 and the thermodynamic dissociation constant $K = 9{\cdot}99 \times 10^{-5}$. The calculated values of K are also shown in Table 2. As in the case of the monochloride, other relationships between Λ_m and C_m corresponding to alternative mechanisms of ionisation were singularly unsuccessful in accounting for the results.

Zirconium Trichloride Monoethoxide.—The most striking feature of the results was the appearance of two intersecting straight lines in the plot of Λ_mC_m against $1/\Lambda_m$, thus recalling the behaviour of lanthanum trichloride.[1] The results at the highest dilution ($C_m = 10^{-5}$—10^{-4}M) gave an apparent limiting molar conductance $\Lambda_0' = 252{\cdot}4$ and $K' = 7{\cdot}67 \times 10^{-5}$ and the data are shown in Table 3.

TABLE 3.

10^5C	Λ_m	$\Lambda_{calc.}$	10^4K	10^5C_m	Λ_m	$\Lambda_{calc.}$	10^4K
0·8347	227·7	229·4	1·76	4·8329	175·1	175·5	2·02
1·3252	219·6	219·6	2·02	5·6770	167·8	168·8	1·98
2·0342	208·7	207·4	2·13	6·5978	162·3	162·5	2·02
2·7400	198·4	197·2	2·12	7·5786	156·4	156·5	2·05
3·4458	188·4	188·9	1·93	8·8614	149·8	149·8	2·01
4·0766	183·5	182·5	2·10	10·336	144·1	143·1	2·04

Alternatively, the assumption of complete solvolysis:

$$\mathrm{ZrCl_3(OEt)} + \mathrm{3EtOH} \longrightarrow \mathrm{Zr(OEt)_4} + \mathrm{3H^+} + \mathrm{3Cl^-} \quad . \quad . \quad . \quad . \quad (7)$$

and application of Fuoss's treatment to *equivalent* conductances and normalities gave the limiting *equivalent* conductance $\Lambda_0 = 85{\cdot}85$ and the thermodynamic dissociation constant $K = 2{\cdot}02 \times 10^{-4}$. Calculated values for K are also given in Table 3. The results for the more concentrated solutions ($C_m = 1{\cdot}8$—$3{\cdot}9 \times 10^{-4}$M) are extremely interesting in resembling those for the *dichloride*. A plot of $\Lambda_m C_m$ against $1/\Lambda_m$ gave a straight line corresponding to an apparent limiting molar conductance $\Lambda_0' = 150{\cdot}1$ (cf. the dichloride 144·1) and $K' = 6{\cdot}96 \times 10^{-4}$. The deviations of Λ_m from $\Lambda_{\text{calc.}}$ showed a percentage standard deviation of $\pm 0{\cdot}15\%$. The data are given in Table 4.

Again the alternative treatment of using *equivalent* conductances (assuming equiv. = $\frac{1}{2}M$) and normalities and applying Fuoss's treatment gave a satisfactory interpretation of the results with the limiting *equivalent* conductance $\Lambda_0 = 79{\cdot}5$ and $K = 1{\cdot}013 \times 10^{-3}$. This behaviour of the trichloride is strongly indicative of successive ionisations and does not support the suggestion of complete solvolysis. The most striking feature of the results for these three compounds is the proximity of Λ_0 in each case to that for hydrochloric acid as shown in the summary of the data in Table 5.

TABLE 4.

C_m	1·8201	2·1292	2·7213	3·8731
Λ_m	123·8	120·5	115·1	107·4
$\Lambda_{\text{calc.}}$	123·5	120·5	115·3	107·3
10^3K	1·017	1·012	1·008	1·017

TABLE 5.

Compound	Λ_0 *	10^5K	Λ_0' †	$10^5K'$
$\mathrm{ZrCl(OEt)_3}$	73·65	9·78	—	—
$\mathrm{ZrCl_2(OEt)_2}$	77·15	9·99	144·1	6·64
$\mathrm{ZrCl_3(OEt)}$ (*a*)	85·85	20·2	252·4	7·67
,, (*b*)	79·5	101·3	150·1	69·6
HCl	82·46	823	—	—

* From equivalent conductances. † From molar conductances.
(*a*) Most dilute region; (*b*) lower dilution.

It is noteworthy that Λ_0 increases steadily from the monochloride to the trichloride whereas if the charged species $\mathrm{Zr(OEt)_3^+}$, $\mathrm{Zr(OEt)_2^{2+}}$, and $\mathrm{Zr(OEt)^{3+}}$ were involved we should expect the opposite trend in Λ_0. Moreover, solvolysis becomes increasingly more probable in passing from the monochloride to the trichloride. It is clear that other experimental work involving a different technique will be required to resolve this complex situation but we are inclined to the view that solvolytic equilibria of the type depicted in eqn. (2) are involved.

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