937. *Chloroalkoxides of Titanium, Zirconium, Cerium, and Thorium.*

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Various methods for preparing metal chloroalkoxides have been explored, including reactions involving a chloroalcohol, chloroaldehyde or a chloroalkyl carboxylate. The following new compounds were prepared: $Ti(OX)_4$; $Zr(OX)_4$; $Ce(OX)_4,C_5H_5N$; $Th(OX)_4,2C_5H_5N$; $TiCl(OX)_3$; $ZrCl(OX)_3$; $Ti(OEt)(OX)_3$; $Ti(OPr^i)(OX)_3$; $Ti(OY)_4$; $Zr(OY)_4,2Me_2CO$ and $Ti(OZ)_4$, where $X = CCl_3{\cdot}CMe_2$, $Y = CCl_3{\cdot}CH_2$, and $Z = CH_2Cl{\cdot}CH_2$. These results throw more light on the mechanism of the reaction of alcohols with metal chlorides and on the structural theory for polymeric metal alkoxides.

A MAJOR problem in interpreting the effect of the alkyl group on the properties of metal alkoxides has been to distinguish between steric and electronic effects.[1, 2] The evidence supporting our view [2] that steric effects predominate is based on the behaviour of a large number of different alkoxides but in particular it turns on the behaviour of the *neo*pentyloxide group. Although the remarkable steric effect of the *neo*pentyl group is well established,[3] there still remains the possibility of transmission of a small amount of the $+I$ inductive effect of the *tert.*-butyl group through the alcoholic carbon. In view of the similarity of the size of the methyl group to that of covalently bound chlorine it seemed likely that suitably chosen chloroalkyl groups would provide a decisive means of testing our theory. For example, the 2 : 2 : 2-trichloroethoxide group will resemble the *neo*pentyloxide group in steric effect but has the opposite electronic inductive effect. This paper deals with the chloroalkoxides of titanium, zirconium, cerium(IV), and thorium; introduction of chlorine into the alkyl group caused some unexpected results.

Tetrakis-1-methyl-1-trichloromethylethoxy-derivatives.—The tetrakis-1-methyl-1-trichloromethylethoxy-derivatives of titanium and zirconium were obtained by alcohol interchange of 1-methyl-1-trichloromethylethanol ("chlorbutol") and the metal *iso*propoxide. Both compounds were monomeric in boiling benzene and the titanium derivative sublimed at 150°/0·15 mm. whilst the zirconium derivative decomposed above *ca.* 130°/0·1 mm. Attempts to prepare the cerium(IV) and thorium derivatives by the same method were unsuccessful, being accompanied by precipitation of decomposition products. In the case of thorium this may be due to the basic character of the *iso*propoxide. However, further work showed that the titanium and zirconium derivatives could also be prepared by the ammonia method involving either the metal chloride [1] or dipyridinium zirconium hexachloride.[4] When the ammonia method was tried with either the complex chlorocerate or the complex chlorothorate, $Ce(O{\cdot}C_4H_6Cl_3)_4,C_5H_5N$ and

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[1] Bradley and Wardlaw, *J.*, 1951, 280.
[2] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027.
[3] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.
[4] Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.

$Th(O{\cdot}C_4H_6Cl_3)_4,2C_5H_5N$ respectively were obtained. Neither compound could be obtained free from addended pyridine and both decomposed at *ca.* 115—120°/0·1 mm. These results show that the presence of chlorine in a tertiary alcohol profoundly affects the reactivity of the alcohol. For example, previous work involving reactions of tertiary alcohols with either the complex zirconium[4] or cerium[5] chlorides in the presence of ammonia showed that chloride alkoxide pyridine adducts $MCl(OR)_3,C_5H_5N$, where $M = Zr$ or Ce^{IV}, were formed. Yet with chlorbutol complete replacement of metal–chlorine bonds occurs. Now, we have found that chlorbutol reacts with either titanium or zirconium tetrachlorides forming the tris-1-methyl-1-trichloromethylethoxy-metal monochlorides $MCl(O{\cdot}C_4H_6Cl_3)_3$, where $M = Ti$ or Zr. The titanium compound was caused to react with ethanol or *iso*propyl alcohol and ammonia and formed the mono-ethoxide and mono*iso*propoxide respectively. It is noteworthy that normal alcohols react with these tetrachlorides to form respectively $TiCl_2(OR)_2,ROH$ and a mixture of $ZrCl_3(OR),ROH$ and $ZrCl_2(OR)_2,ROH$, but tertiary alcohols are involved in a more complex reaction which results in the hydrolysis of the metal compounds. This contrast in behaviour between chlorbutol and unsubstituted tertiary alcohols in their reactions with metal chlorides shows clearly the influence of the electronic effects of the alkyl groups on the reactivity of alcohols with metal chlorides. In an earlier paper[6] we suggested that part of the " driving force " for the reaction between metal chloride and an alcohol is the induced positive charge ($\delta+$) on the metal caused by the electronegative chlorine atoms (*viz.*, $\overset{\delta+}{M}\text{–}\overset{\delta-}{Cl}$), and that replacement of the chlorine by the less electronegative alkoxide groups reduces this driving force and ultimately prevents further replacement. The behaviour of chlorbutol agrees with this hypothesis because the ($-I$) effect of the trichloromethyl group makes the 1-methyl-1-trichloromethyl-ethoxide group more electronegative than a normal alkoxide group and the ($\delta+$) on the metal is sustained through a greater degree of replacement of M–Cl bonds.

From the steric viewpoint the 1-methyl-1-trichloromethylethoxide group resembles the 1 : 1 : 2 : 2-tetramethylpropoxide group and it is noteworthy that the volatilities of the titanium derivatives of the former (150°/0·15 mm.) and the latter (163°/0·5 mm.) are very similar and both compounds are monomeric.

Tetrakis-2 : 2 : 2-*trichloroethoxy-derivatives.*—To explore the scope of preparative methods for metal chloroalkoxides we tried the Meerwein–Ponndorf–Verley reaction of 1 : 1 : 1-trichloroacetaldehyde (" chloral ") with the metal alkoxides. With titanium *iso*propoxide the following reaction occurred:

$$Ti(OPr^i)_4 + 4Cl_3C{\cdot}CHO \longrightarrow Ti(O{\cdot}CH_2{\cdot}CCl_3)_4 + 4Me_2CO$$

The titanium tetrakis-2 : 2 : 2-trichloroethoxide had a degree of polymerisation of 1·5, close to that (1·3) for titanium tetra*neo*pentyloxide, in boiling benzene. This clearly emphasises the major importance of steric effects in the influence of chain-branching on physicochemical properties of the metal alkoxides. Thus the similar size and shape of the 2 : 2 : 2-trichloroethoxide and *neo*pentyloxide groups means that from steric considerations alone their titanium derivatives should have the same degree of polymerisation. On the other hand the $-I$ inductive effect of the trichloromethyl group compared with the $+I$ effect of the *tert.*-butyl group causes the 2 : 2 : 2-trichloroethoxide group to be more electronegative than the *neo*pentyloxide group, and the titanium derivative of the former will have a higher ($\delta+$) than that of the latter. The derivative with the higher ($\delta+$) on its titanium atom will have the greater tendency to polymerise through intermolecular bonding. When zirconium *iso*propoxide was treated with chloral under similar conditions half of the acetone produced in the reaction was retained by co-ordination with the zirconium in the compound $Zr(O{\cdot}CH_2{\cdot}CCl_3)_4,2Me_2CO$. Attempts to remove the acetone

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[5] Bradley, Chatterjee, and Wardlaw, *J.*, 1957, 2600.

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

were unsuccessful owing to decomposition of the compound at 100°/0·1 mm. This compound is of special interest because it is another example of a co-ordination compound involving a zirconium alkoxide. These are rare because the metal alkoxide prefers to co-ordinate through an alkoxide group from a neighbouring molecule to form a polymer. In fact most attempts to form co-ordination compounds with zirconium alkoxides have failed. Even zirconium tetra*iso*propoxide, which co-ordinates with pyridine or *iso*propyl alcohol, would not co-ordinate with diethyl ether, triethylamine, thiourea, ethylenediamine, or αα′-dipyridyl. However, the tetrachloride, trichloride monoethoxide, dichloride diethoxide, dichloride di*iso*propoxide, or monochloride tri*iso*propoxide of zirconium forms some stable complexes and it appears that the combination of an electronegative group with the zirconium is a necessity for complex formation. This may well explain the behaviour of zirconium tetrakis-2 : 2 : 2-trichloroethoxide. When either cerium(IV) or thorium *iso*propoxide was treated with chloral the Meerwein–Ponndorf–Verley reaction was complicated by side reactions and the tetrakis-2 : 2 : 2-trichloroethoxides could not be obtained. In the case of thorium this may be due to the basic character of thorium *iso*propoxide.

Tetrakis-2-chloroethoxy-derivatives.—Since metal alkoxides undergo transesterification with organic esters it seemed worth while to try to prepare a chloroalkoxide by this method. Titanium tetra*iso*propoxide reacted with 2-chloroethyl acetate according to the equation:

$$\mathrm{Ti(OPr^i)_4 + 4CH_3{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow Ti(O{\cdot}CH_2{\cdot}CH_2Cl)_4 + 4CH_3{\cdot}CO_2Pr^i}$$

However, zirconium *iso*propoxide appeared not to react at a significant rate with 2-chloroethyl acetate.

EXPERIMENTAL

Materials.—The complex chlorides and the *iso*propoxides of titanium, zirconium, cerium(IV), and thorium were prepared by the methods already described.[2, 4, 7, 8] "Chlorbutol" and 2-chloroethyl acetate were dried azeotropically with benzene containing *ca.* 3% of *iso*propyl alcohol. Chloral was shaken with sulphuric acid (conc.), separated, and then distilled. Special precautions were taken throughout to avoid hydrolysis and reactions were conducted in an atmosphere of oxygen-free nitrogen. Analyses and molecular-weight determinations were carried out as described previously.[2, 4, 7, 8]

Reactions of Titanium Tetrachloride or Zirconium Tetrachloride with "Chlorbutol."—Chlorbutol (55 g.), added to titanium tetrachloride (12 g.) in carbon tetrachloride (200 c.c.), caused a vigorous reaction. After 8 hours' refluxing, the volatile products and solvent were evaporated off, leaving *tris*-1-*methyl*-1-*trichloromethylethoxytitanium monochloride* as a white solid (34 g.) [Found: Ti, 7·86%; *M*, 611·8. $\mathrm{TiCl(OC_4H_6Cl_3)_3}$ requires Ti, 7·82%; *M*, 612·9]. From a similar reaction of the tetrachloride (11 g.) and chlorbutol (50 g.) in benzene (200 c.c.), the product (30 g.) had the analysis: Ti, 8·1; C, 23·4; H, 3·39; Cl, 61. $\mathrm{TiCl(OC_4H_6Cl_3)_3}$ requires Ti, 7·82; C, 23·5; H, 2·94; Cl, 57·9%. A sample of the foregoing product heated in a short-path still sublimed at 105—110°/0·1 mm. (Found for the sublimate: Ti, 7·85%). The compound (12 g.) in carbon tetrachloride (250 c.c.) was treated with ethanol (1·0 g.) and ammonia. Ammonium chloride was filtered off and the filtrate on evaporation under reduced pressure left a white solid (11·8) [Found: Ti, 7·65; EtO, 7·08%; *M*, 635. $\mathrm{Ti(OEt)(OC_4H_6Cl_3)_3}$ requires Ti, 7·69; EtO, 7·23%; *M*, 622·4]. *Tris*-1-*methyl*-1-*trichloromethylethoxytitanium monoethoxide* sublimed at 160°/0·1 mm. (Found for the sublimate: Ti, 7·68%). Similarly, *tris*-1-*methyl*-1-*trichloromethylethoxytitanium mono*iso*propoxide* was obtained from the reaction involving the monochloride (10 g.), *iso*propyl alcohol (0·995 g.), and ammonia in carbon tetrachloride (250 c.c.) as a gum (8 g.) [Found: Ti, 7·53; $\mathrm{Pr^iO}$, 8·60%; *M*, 640. $\mathrm{Ti(OPr^i)(OC_4H_6Cl_3)_3}$ requires Ti, 7·53; $\mathrm{Pr^iO}$, 9·27%; *M*, 636·4]. The mono*iso*propoxide gave volatile products at 125°/0·1 mm. but the condensate (Found: Ti, 8·2%) was not the mono*iso*propoxide. "Chlorbutol" (38 g.), added to a suspension of zirconium tetrachloride (10 g.) in benzene (200 c.c.), caused a vigorous reaction with evolution of hydrogen chloride. After 9 hours' refluxing the volatile

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[7] Bradley, Chatterjee, and Wardlaw, *J.*, 1956, 2260.

[8] Bradley, Saad, and Wardlaw, *J.*, 1954, 1091.

products and solvent were evaporated off under reduced pressure and left a gum (24 g.) [Found: Zr, 14·1%; *M*, 651. $ZrCl(OC_4H_6Cl_3)_3$ requires Zr, 13·9%; *M*, 656].

Reactions involving Chlorbutol, Metal Chlorides, and Ammonia.—These were conducted by our standard procedures and the results are in Table 1.

Reactions of Chlorbutol with Metal iso*Propoxides*.—Chlorbutol was added to the benzene solution of the metal *iso*propoxide and the liberated *iso*propyl alcohol was removed by azeotropic fractionation. The solvent was then evaporated off under reduced pressure. The results are in Table 2.

TABLE 1.

Metal chloride taken	Chlorbutol (g.)	Benzene (c.c.)	Product	Analysis Found	Analysis Calc.
$TiCl_4$ (11 g.)	50	200	$Ti(OC_4H_6Cl_3)_4$ (35 g.)	Ti, 6·37%; *M*, 760	Ti, 6·35%; *M*, 754
$ZrCl_4$ (8 g.)	35	200	$Zr(OC_4H_6Cl_3)_4$ (20 g.)	Zr, 11·3; C, 24·2; H, 3·92; Cl, 52·0%; *M*, 802	Zr, 11·4; C, 24·1; H, 3·01; Cl, 53·4%; *M*, 797
$(C_5H_6N)_2ZrCl_6$ (10 g.)	25	250	$Zr(OC_4H_6Cl_3)_4$ (10·5 g.)	Zr, 11·2%	Zr, 11·4%
$(C_5H_6N)_2CeCl_6$ (12 g.)	25	200	$Ce(OC_4H_6Cl_3)_4,C_5H_5N$ (14 g.)	Ce, 15·3; C, 29·5; H. 3·3%	Ce, 15·15; C, 27·2; H, 3·1%
$(C_5H_6N)_2ZrCl_6$ (8 g.)	20	200	$Th(OC_4H_6Cl_3)_4,2C_5H_5N$ (10 g.)	Th, 21·4; C, 28·3; H, 3·67; Cl, 37·9; N, 2·0%	Th, 21·2; C, 28·5; H, 3·1; Cl, 38·8; N, 2·5%

TABLE 2.

Metal *iso*propoxide taken	Chlorbutol (g.)	Benzene (c.c.)	Product (g.)	Analysis Found	Analysis Calc.*
$Ti(OPr^i)_4$ (10 g.)	30·0	250	20·5	Ti, 6·36%; *M*, 755	Ti, 6·35%; *M*, 754
$Zr(OPr^i)_4,Pr^iOH$ (7 g.) ...	20·0	250	12	Zr, 11·5%; *M*, 798	Zr, 11·4%; *M*, 797
$Ce(OPr^i)_4,Pr^iOH$ (8 g.) ...	18·5	250	6·0	Ce, 41·9%	Ce, 16·5%
$Th(OPr^i)_4$ (8 g.)	25·0	250	9·0	Th, 39·0%	Th, 24·7%

* Calc. for metal tetrakis-2 : 2 : 2-trichloroethoxide.

Titanium Tetrakis-2 : 2 : 2-trichloroethoxide.—Chloral (18 g.) was added to titanium *iso*propoxide (8 g.) in benzene (200 c.c.). The mixture was fractionally distilled until no more acetone was collected and the solvent was then evaporated off under reduced pressure leaving a solid (15 g.) [Found: Ti, 7·60%; *M*, 962·5. $Ti(OC_2H_2Cl_3)_4$ requires Ti, 7·50%; *M*, 642]. Attempts to sublime the *compound* led to decomposition (Found for the residue: Ti, 9·65%).

Bisacetone Adduct of Zirconium Tetrakis-2 : 2 : 2-trichloroethoxide.—Chloral (20 g.) and zirconium tetra*iso*propoxide (10 g.) in benzene (200 c.c.) were fractionally distilled until the liberation of acetone ceased. Removal of solvent under reduced pressure left a solid (18 g.) [Found: Zr, 11·5; C, 21·0; H, 2·2; Cl, 55·0. $Zr(OC_2H_2Cl_3)_4,2Me_2CO$ requires Zr, 11·4; C, 21·0; H, 2·5; Cl, 53·2%]. The *compound* retained its addenda up to 100°/0·1 mm. (Found: Zr, 11·8%) but did not sublime. The presence of acetone was proved by treating a sample with sulphuric acid (2N) and testing the distillate with 2 : 4-dinitrophenylhydrazine.

Titanium Tetrakis-2-chloroethoxide.—Titanium *iso*propoxide (10 g.) and 2-chloroethyl acetate (20 g.) were caused to react in boiling benzene (250 c.c.). Fractional distillation was carried out until no more *iso*propyl acetate was liberated. Evaporation of the solvent under reduced pressure left a viscous liquid (11·3 g.) [Found: Ti, 13·0. $Ti(CO_2H_4Cl)_4$ requires Ti, 13·2%]. In a similar reaction of zirconium *iso*propoxide with 2-chloroethyl acetate no *iso*propyl acetate was detected after prolonged fractional distillation and the zirconium compound (Found: Zr, 25·4%) which was recovered from solution was not the tetrakis-2-chloroethoxide.

*Addition of Donor Molecules to Zirconium Tetra*iso*propoxide*.—In separate experiments diethyl ether, triethylamine, thiourea, ethylenediamine, and αα′-dipyridyl were added to zirconium tetra*iso*propoxide in benzene in the molar ratio of 4 : 1 respectively. No crystalline products were formed and evaporation of the solutions under reduced pressure left the tetra*iso*propoxide in each case.

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