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Oxozirconium(IV) Alkoxides

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Oxozirconium(IV) alkoxides of the type $ZrO(OR)_2 \cdot ROH$ and $ZrOCl(OR) \cdot 2\,ROH$, where R is methyl, ethyl, and isopropyl, and $ZrO(OCMe_3)_2 \cdot 0.5\,Me_3COH$ and $ZrOCl(OCMe_3) \cdot$ $\cdot\, 1.5\,Me_3COH$ have been prepared by the reaction of dichloroxozirconium(IV)-2-acetic acid with corresponding alcohols in the presence of appropriate amounts of piperidine. The alkoxides have been isolated and characterised through infrared, thermal and conductance studies.

Introduction

Zirconium(IV) alkoxides are well known[1–3] but the corresponding compounds of oxozirconium(IV) have not so far been reported. The present work has the object of isolation and characterisation of oxozirconium(IV) alkoxides and monochloroxozirconium(IV) alkoxides.

Experimental

$ZrOCl_2 \cdot 8\,H_2O$ (Fluka AG, prakt.) was treated with hot water, filtered and the filtrate was mixed with a small amount of acetone to crystallise out $ZrOCl_2 \cdot 8\,H_2O$. It was recrystallised from its hot solution in HCl.

The addition compound $ZrOCl_2 \cdot 2\,MeCO_2H$ was prepared by the action of CH_3COCl on $ZrOCl_2 \cdot 8\,H_2O$ at low temperature[4]. All the alcohols were dried by refluxdistilling over the corresponding sodium alkoxides. The middle fractions were taken for use.

Infrared measurements were made on Perkin-Elmer 621. Samples were run in nujol and HCB using NaCl and polythene plates and also as KBr pellets. Thermal analysis was done on Derivatograph MOM, Budapest.

Zirconium was estimated as ZrO_2 after heating the compound upto 900°. Chlorine was determined as AgCl. Carbon and hydrogen were analysed microanalytically.

Preparation of Alkoxides

$ZrO(OMe)_2 \cdot MeOH$

$ZrOCl_2 \cdot 2\,MeCO_2H$ (10 mMoles) was dissolved in 15 ml of *Me*OH and piperidine (20 mMoles) was added dropwise under constant stirring. The precipitate was filtered, washed with *Me*OH. The residue was dried for 3–4 h under high vac. The white solid is insoluble in alcohols, CH_2Cl_2, $CHCl_3$, nitromethane, nitrobenzene, acetonitrile and *THF*.

$ZrO(OEt)_2 \cdot EtOH$

It was prepared as above except that the precipitate was washed with $CHCl_3$ in order to remove piperidinium chloride completely.

$ZrO(OPr^i)_2 \cdot Pr^iOH$

$ZrOCl_2 \cdot 2\,MeCO_2H$ (10 mMoles) was dissolved in hot isopropyl alcohol (20 ml) and piperidine (20 mMoles) was added dropwise with constant stirring. Piperidinium chloride was precipitated with 20 ml of petroleum ether (*PÄ*). The rest of the procedure was as above. Recrystallisation from a mixture of isopropyl alcohol and *PÄ*.

$ZrO(OCMe_3)_2 \cdot 0.5\,Me_3COH$

$ZrOCl_2 \cdot 2\,MeCO_2H$ (10 mMoles) was treated in boiling *t*-butyl alcohol (40 ml) with piperidine (20 mMoles) as above. The piperidinium chloride was filtered and the filtrate was treated as in other cases.

$ZrOCl(RO) \cdot x ROH$

The monochloro derivatives were prepared and isolated like their corresponding disubstituted alkoxides, except that piperidine in molar ratio of 1 : 1 was added slowly with constant stirring to the solution of $ZrOCl_2 \cdot \cdot 2\,MeCO_2H$ in the parent alcohol. Higher alkoxides can be recrystallised from a mixture of the parent alcohol and *PÄ*.

The elemental analyses of the compounds are given in Table 1. All the compounds were handled on a vacuum line and in an atomsphere of dry nitrogen gas.

Results and Discussion

In the compound, $ZrOCl_2 \cdot 2\,MeCO_2H$, the solvated acetic acid molecules can be replaced by nitrogen and oxygen bases stronger than acetic acid[5]. This compound is insoluble in most of the polar organic solvents but dissolves in alcohols (solubility decreases with higher alcohols). If refluxed in alcohols, partial replacement of chloride by alkoxy group takes place but compounds of definite compositions are difficult to obtain. The alcoholic solutions of $ZrOCl_2 \cdot 2\,MeCO_2H$, if treated with piperidine in a molar ratio of 1 : 2, give compounds $ZrO(OR)_2 \cdot ROH$, where R is CH_3, C_2H_5 and $i\text{-}C_3H_7$, and $ZrO(OCMe_3)_2 \cdot \cdot 0.5\,Me_3COH$. Attempts to remove the solvated molecules of alcohols under high vacuum failed. Treatments with strong bases like triethylamine and pyridine, too, did not affect replacement. The compounds appear to be coordinatively saturated and polymeric like most other compounds of oxozirconium(IV). Lower alkoxides are insoluble in nitromethane, nitrobenzene, chloroform, dichloromethane, etc., but the higher ones appear to have some solubility in these solvents. The molar conductance values (Table 1) show that the compounds are almost nonconducting in solutions.

Compounds of compositions $\mathrm{ZrOCl(OR)} \cdot 2\,\mathrm{ROH}$, where R is CH_3, C_2H_5, and i-C_3H_7 and $\mathrm{ZrOCl(OC}\mathit{Me}_3) \cdot 1.5\,\mathit{Me}_3\mathrm{COH}$ are formed when $\mathrm{ZrOCl_2} \cdot 2\,\mathit{Me}\mathrm{CO_2H}$ in excess alcohols is treated with piperidine in the molar ratio of 1 : 1. The compounds, especially higher analogues, are more soluble than the dialkoxides. The solvated alcohols are replacable[5]. The molar conductance values show that these, too, are nonelectrolytes (Table 1).

Table 1. *Elemental Analysis and Molar Conductance Values*

Compound	$\Lambda^* \cdot 1000$	Analysis, Found (Calcd.) %			
	25°	Zr	C	H	Cl
$\mathrm{ZrO(O}\mathit{Me})_2 \cdot \mathit{Me}\mathrm{OH}$	—	44.4 (45.3)	17.6 (17.9)	4.3 (5.0)	—
$\mathrm{ZrO(}\mathit{E}\mathrm{O}\mathit{t})_2 \cdot \mathit{Et}\mathrm{OH}$	—	37.2 (37.5)	28.5 (29.6)	6.2 (6.6)	—
$\mathrm{ZrO(O}\mathit{Pr}^i)_2 \cdot \mathit{Pr}^i\mathrm{OH}$	—	31.5 (32.0)	37.1 (37.9)	7.0 (7.7)	—
$\mathrm{ZrO(O}\mathit{Bu}^t)_2 \cdot 0.5\,\mathit{Bu}^t\mathrm{OH}$	6.6**	31.1 (31.4)	40.2 (41.3)	7.8 (7.9)	—
$\mathrm{ZrOCl(O}\mathit{Me}) \cdot 2\,\mathit{Me}\mathrm{OH}$	0.8***	38.0 (38.4)	14.8 (15.1)	4.4 (4.6)	14.0 (14.9)
$\mathrm{ZrOCl(O}\mathit{Et}) \cdot 2\,\mathit{Et}\mathrm{OH}$	1.6***	32.2 (32.6)	25.1 (25.7)	5.8 (6.1)	12.0 (12.7)
$\mathrm{ZrOCl(O}\mathit{Pr}^i) \cdot 2\,\mathit{Pr}^i\mathrm{OH}$	1.8***	28.1 (28.4)	33.1 (33.6)	6.9 (7.2)	10.7 (11.0)
$\mathrm{ZrOCl(O}\mathit{Bu}^t) \cdot 1.5\,\mathit{Bu}^t\mathrm{OH}$	1.5***	27.5 (27.9)	35.9 (36.7)	7.1 (7.3)	10.2 (10.9)

* $cm^2\ ohm^{-1}\ mole^{-1}$.
** In nitrobenzene.
*** In nitromethane.

The principal infrared bands and their assignments are given in Table 2. A broad band of medium intensity due to the stretching mode of hydroxyl group of ROH appears in the region 3500–3100 cm^{-1}. A bending mode δ OH in the simple solvates is usually assigned in the 1450 cm^{-1} region[6]. In the present investigations, all compounds have been found to show medium intensity broad bands at ca. 1550 cm^{-1}. This band is difficult to assign to any other vibrational mode of the oxozirconium(IV) alkoxide and has tentatively been associated with δ OH of the solvated ROH. On comparison of the spectra of pure alcohols and alkoxides in the present work and already reported data[2, 3, 6], the bands due to ν CO of OR and ROH have been assigned at ca. 1145 to

1050 cm^{-1} and 1030–1025 cm^{-1}, respectively (Table 2). As per nature of zirconium and the positions of ν CO[7, 8], the alkoxide groups are expected to be bridged.

In the infrared spectra of transition metal oxyhalides, sharp intense bands in the region 950–1100 cm^{-1} are usually fixed as a criteria to determine the existence of $M = O$ entity[9]. Medium intensity bands in the region 800–950 cm^{-1} are assigned to zirconium—oxygen vibrations of bonds with order appreciably greater than one but less than two[10].

Table 2. *Important Infrared Bands* (cm^{-1}) *and Their Assignments*

Assignment	Compound *							
	a	e	b	f	c	g	d	h
ν OH	3500— 3100 mb	3500— 3100 mb	3500— 3250 mb	3500— 3250 mb	3500— 3150 mb	3500— 3100 mb	3500— 3100 m	3500— 3100 mb
δ OH (ROH) ?	1565 mb	1540 mb	1560 mb	1550 mb	1565 mb	1560 mb	1555 mb	1560 mb
ν CO (OR)	1145 m	1160 m	1160 m	1160 m	1050 m	1050 m	1040 shb	1050 sh
ν CO (ROH)	1050 s	1023 s	1025 s	1025 s	1030 s	1030 s	1026 s	1030 s
ν Zr—O—Zr	648 m	650 m	650 m	648 m	652 m	650 m	650 m	650 m
ν Zr—O	500 m, 450 s	510 m, 460 s	528 m, 455 s	500 sh, 452 s	535 m, 468 s	528 m, 465 s	535 m, 480 m	550 m, 475 m
ν Zr—Cl	—	363 m, 319 w	—	382 m, 350 w, 295 w	—	390 m, 298 w	—	330 w, 290 w

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* For complete formulas refer Scheme 1.
s = strong, sh = shoulder, m = medium, mb = medium broad, w = weak.

On comparing the complete spectra of alkoxides with those of pure alcohols, there are no bands in the 1000–700 cm^{-1} region which could exclusively be assigned to oxozirconium group. New bands observed at ca. 650 cm^{-1} in the spectra of complexes are most likely due to the polymeric chains Zr—O—Zr—. A bonding of this type is reported in dichloroxozirconium(IV)[11] and $ZrO(HCO_2)_2 \cdot 2\,H_2O$[12] where ν Zr—O— have been reported at 675 cm^{-1} and 650 cm^{-1}, respectively. Further bands due to ν Zr—OR have been observed at ca. 500 cm^{-1} and 450 cm^{-1}. Bands located at ca. 380 cm^{-1} and 290 cm^{-1} in the monochloro derivatives but missing totally in the disubstituted derivatives, have been assigned to ν Zr—Cl (Table 2).

The compounds $ZrO(OR)_2 \cdot ROH$ do not lose the solvated ROH. In view of this and on the basis of the tendency of zirconium to form hydroxides, these may be formulated as $Zr(OH)(OR)_3$. The hydroxides of zirconium give wide bands at about 1100 cm^{-1} or below[13] but no such bands characteristic of δ Zr—OH have been observed. Further, unlike the present compounds, the ν OH in the hydroxides is normally sharp. In addition, taking into account the nature of monochloro derivatives (where solvated alcohols can be replaced), it is very unlikely that the compounds exist as hydroxides.

Both the types of alkoxides are fairly stable and their thermal analyses have been carried out in the presence of air. The t.g., d.t.g., and d.t.a. show the thermal decompositions as processes consisting of several steps. The d.t.g. and d.t.a. curves have been left out as such but the d.t.g. minimas have been used to show clearly the various inflexion points and to determine the extent of weight changes belonging to each step.

The probable modes of decompositions resulting from these curves are given in Scheme 1. The numerator on arrow heads indicate observed weight loss for that step which agrees well with theoretically required values given in parenthesis. The denominator shows the probable molecules eliminated and the temperature range in which loss takes place. The last endothermic step in each case involves a slow loss of water from $ZrO(OH)_2$ to form ZrO_2 in the 400–750° temperature range.

The compound $ZrO(OMe)_2 \cdot MeOH$ (Scheme 1) was also heated separately under vacuum (10^{-3} torr) in the temperature range 150 to 300° and the residue and the liquids trapped were examined separately. The infrared spectrum of the residue shows the appearance of new broad band in the range 1050–1000 cm^{-1} (δ Zr—OH)[13] showing, thereby, the probable formation of hydroxide. The liquid trapped is mostly volatile at room temperature and only traces of some olefin have been indicated alongwith substantial amount of water. No free alcohol is eliminated. The ethoxide decomposes similarly except that the second step involves a loss of ether perhaps. The isopropoxide decomposition (Scheme 1) has been shown to involve losses equivalent to isopropyl ether and C_3H_6. But if heated at 300°/10^{-3} torr, the volatile fractions indicate mainly an olefin (nonvolatile at room temperature) containing small amounts of an aldehyde but no parent alcohol. Similar is the case with *t*-butoxide when heated under vacuum except that it does show some traces of alcohol, too. The compound $ZrOCl(OMe) \cdot 2\,MeOH$ loses a molecule of HCl endothermally to give $ZrO(OMe)_2 \cdot MeOH$ which then decomposes as indicated already. The loss of HCl has been confirmed by heating the compound at 150°/10^{-3} torr. The ethoxide shows a simultaneous loss of HCl and water endothermally. In the cases of isopropoxide and *t*-butoxide, no free HCl is liberated. The former involves a probable elimination of isopropyl chloride between

Scheme 1. *Thermal decomposition patterns of alkoxides*

a $$\mathrm{ZrO(O}Me\mathrm{)_2 \cdot }Me\mathrm{OH} \xrightarrow[\mathrm{-C_3H_6\ (80-300^\circ)}]{20.7\ (20.9\%)} \mathrm{ZrO(OH)_2 \cdot H_2O} \xrightarrow[\mathrm{-H_2O\ (300-400^\circ)}]{29.7\ (29.8\%)}$$
$$\mathrm{ZrO_2} \xleftarrow[\mathrm{-H_2O\ (400-740^\circ)}]{38.9\ (38.8\%)} \mathrm{ZrO(OH)_2} \longleftarrow$$

b $$\mathrm{ZrO(O}Et\mathrm{)_2 \cdot }Et\mathrm{OH} \xrightarrow[\mathrm{-C_4H_8\ (70-270^\circ)}]{22.9\ (23.0\%)} \mathrm{ZrO(OH)_2 \cdot }Et\mathrm{OH}$$
$$\xleftarrow[\mathrm{-\tfrac{1}{2}\ H_2O\ (360-410^\circ)}]{42.0\ (41.9\%)} \mathrm{ZrO(OH)_2 \cdot \tfrac{1}{2}\,H_2O} \xleftarrow[\mathrm{-\tfrac{1}{2}\ }Et_2\mathrm{O\ (270-360^\circ)}]{38.3\ (38.2\%)}$$
$$\mathrm{ZrO(OH)_2} \xrightarrow[\mathrm{-H_2O\ (410-700^\circ)}]{49.2\ (49.3\%)} \mathrm{ZrO_2}$$

c $$\mathrm{ZrO(O}Pr^i\mathrm{)_2 \cdot }Pr^i\mathrm{OH} \xrightarrow[\mathrm{-(C_3H_7)_2O\ (40-270^\circ)}]{35.5\ (35.8\%)} \mathrm{ZrO(OH)(O}Pr^i\mathrm{)}$$
$$\mathrm{ZrO_2} \xleftarrow[\mathrm{-H_2O\ (400-740^\circ)}]{56.8\ (56.8\%)} \mathrm{ZrO(OH)_2} \xleftarrow[\mathrm{-C_3H_6\ (270-400^\circ)}]{50.3\ (50.5\%)}$$

d $$\mathrm{ZrO(O}Bu^t\mathrm{)_2 \cdot 0.5\ }Bu^t\mathrm{OH} \xrightarrow[\mathrm{-\tfrac{1}{2}(C_4H_9OH)\ (40-160^\circ)}]{12.8\ (12.8\%)} \mathrm{ZrO(O}Bu^t\mathrm{)_2}$$
$$\xleftarrow[\mathrm{-H_2O\ (400-800^\circ)}]{57.4\ (57.4\%)} \mathrm{ZrO(OH)_2} \xleftarrow[\mathrm{-2C_4H_8\ (160-400)}]{51.3\ (51.3\%)}$$
$$\rightarrow \mathrm{ZrO_2}$$

e $$\mathrm{ZrOCl(O}Me\mathrm{) \cdot 2\ }Me\mathrm{OH} \xrightarrow[\mathrm{-HCl,\ (50-210^\circ)}]{15.4\ (15.3\%)} \mathrm{ZrO(O}Me\mathrm{)_2 \cdot }Me\mathrm{OH}$$

f $$\mathrm{ZrOCl(O}Et\mathrm{) \cdot 2\ }Et\mathrm{OH} \xrightarrow[\mathrm{-HCl,\ -H_2O\ (60-210^\circ)}]{19.4\ (19.5\%)} \mathrm{ZrO(O}Et\mathrm{)_2 \cdot C_2H_4}$$
$$\mathrm{ZrO(OH)_2} \xleftarrow[\mathrm{-C_2H_4,\ -C_4H_8\ (210-400^\circ)}]{49.3\ (49.5\%)}$$
$$\xrightarrow[\mathrm{-H_2O\ (400-760^\circ)}]{55.8\ (56.0\%)} \mathrm{ZrO_2}$$

g $$\mathrm{ZrOCl(O}Pr^i\mathrm{) \cdot 2\ }Pr^i\mathrm{OH} \xrightarrow[\mathrm{-C_3H_7Cl\ (50-220^\circ)}]{24.6\ (24.4\%)} \mathrm{ZrO(O}Pr^i\mathrm{)(OH)(}Pr^i\mathrm{OH)}$$
$$\mathrm{ZrO_2} \xleftarrow[\mathrm{-H_2O\ (440-760^\circ)}]{62.2\ (61.7\%)} \mathrm{ZrO(OH)_2} \xleftarrow[\mathrm{-Organic\ matter\ (220-440^\circ)}]{56.4\ (56.1\%)}$$

h $$\mathrm{ZrOCl(O}Bu^t\mathrm{) \cdot 1.5\ (}Bu^t\mathrm{OH)} \xrightarrow[\mathrm{-Organic\ matter\ (80-400^\circ)}]{56.8\ (56.8\%)} \mathrm{ZrO(OH)_2}$$
$$\mathrm{ZrO_2} \xleftarrow[\mathrm{-H_2O\ (400-760^\circ)}]{62.3\ (62.3\%)}$$

50–220° also supported by heating under vacuum. The liquids trapped in all the cases indicate the presence of some olefins.

It may be inferred that piperidine works as a very convenient reagent to prepare partially or completely substituted oxozirconium(IV) alkoxides. The molecules of the type $\mathrm{ZrO(OR) \cdot ROH}$ do not form addition compounds and the solvated alcohol is firmly held. This is not true in the cases of $\mathrm{ZrOCl(OR) \cdot 2\,ROH}$.

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