Zirconium and Oxozirconium(IV) Formates

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Tetraformatozirconium(IV), Diformatoxozirconium(IV)dihydrate, Thermogravimetry, IR Spectra

Tetraformatozirconium(IV), Zr(OOCH)4 and diformatoxozirconium(IV)dihydrate, ZrO(OOCH)2 • 2 H2O have been prepared by the reactions of tetrachlorozirconium(IV) and dichlorozirconium(IV) with anhydrous formic acid, respectively. The compounds have been characterized by elemental analyses, molar conductance, thermogravimetry and infrared spectral data. The compounds are nonelectrolytes in nitrobenzene and have polymeric structures.

Reactions of monocarboxylic acids with tetrachlorozirconium(IV) to yield tetracarboxylatozirconium(IV)1, 2 and the mixed derivatives such as ZrX(OOCR)3, ZrX2(OOCR)2 and ZrX3(OOCR) where (X = Cl and R = H, C2H5 and HOCH2CH3) have been reported3. Although reactions of various monocarboxylic acids with dichlorozirconium(IV)-octahydrate, ZrOCl2 • 8 H2O have been studied in aqueous systems4-8, the reaction between anhydrous dichlorozirconium(IV) and carboxylic acids have not yet been thoroughly studied. Only recently PAUL et al.9 have reported the isolation of a new acetate, ZrO(OOCCH2)2 • CH2COOH by the reaction of anhydrous ZrOCl2 with acetic acid. In this communication we report the preparation and characterization of tetraformatozirconium(IV), Zr(OOCH)4 and diformatoxozirconium(IV)dihydrate, ZrO(OOCH)2 • 2 H2O.

Experimental

Reagents: Anhydrous dichlorozirconium(IV) was prepared by the action of thionyl chloride on ZrOCl2 • 8 H2O10. Tetrachlorozirconium(IV) (Fluka) was used as such. Anhydrous formic acid was prepared from (98–100% BDH) sample by the method given by POPOV et al.11.

General procedure for the preparation of compounds: Tetrachlorozirconium(IV) and anhydrous ZrOCl2 were refluxed with excess of anhydrous formic acid for about 4–5 hours till the evolution of HCl gas had completely ceased. The supernatant liquid was decanted, the white crystalline products were filtered, washed with dichloromethane and dried under reduced pressure.

Elemental analysis: Zirconium was estimated as ZrO2 by heating the compounds to a constant weight above 700 °C. Carbon and hydrogen were analysed microanalytically.

Infrared measurements of the compounds were made on Perkin-Elmer IR models 337 and 521 using KBr pellets and as nujol mulls.

Thermogravimetric analysis was carried out on a Stanton Thermobalance Model TR-1. Thermograms were obtained on 300–400 mg samples at a heating rate of 4° min⁻¹.

Results and Discussion

The analytical results along with melting points, solubilities and molar conductance data of the compounds Zr(OOCH)4 and ZrO(OOCH)2 • 2 H2O are given in Table I. All attempts to prepare the earlier reported3 mixed derivatives of the type ZrXₙ(OOCR)₄₋ₙ (where n = 1, 2 and 3) even with limited quantities have resulted in mixtures of the completely substituted product and the parent compound. The reaction of anhydrous ZrOCl2 with formic acid always yields the product ZrO(OOCH)2 • 2 H2O and attempts to prepare the dehydrated product ZrO(OOCH)2 have been unsuccessful. It is obvious that the water molecules are strongly bonded to the Zr atom. It seems that the anhydrous formate ZrO(OOCH)2 once formed takes up two molecules of water from formic acid as is already known in the case of vanadyl formate, VO(OOCH)2 • H2O.12

Both these compounds are stable to moisture. The molar conductances of the millimolar solutions...
of compounds in nitrobenzene indicate their covalent nature (Table I). Both Zr(OOCH)₄ and ZrO(OOCH)₂ · 2 H₂O do not form addition compounds with strong bases such as pyridine or triethylamine. This may be taken to indicate that Zr atom in these compounds is coordinately saturated. It is significant to note that the compound ZrO(OOCCCH₃)₂ · CH₃COOH forms several oxo-zirconium(IV) complexes of the type ZrO(An)₂, ZrO(Gly)₂⁹ whereas similar reactions with ZrO(OOCH)₂ · 2 H₂O always yield the parent compound.

The important characteristic vibrational bands of the compounds are recorded in Table II. The difference between the νₐₚₚ and νₚₚ vibrations of the COO⁻ groups has been generally employed to characterize the nature of bonds between the formate group and the metal¹³. The spectra of these compounds show intense absorption bands for ν(COO⁻)ₚₚ at (1555 cm⁻¹ for Zr(OOCH)₄ and 1525 cm⁻¹ for ZrO(OOCH)₂ · 2 H₂O and ν(COO⁻)ₚₚ at (1360 cm⁻¹ for Zr(OOCH)₄ and 1345 cm⁻¹ for ZrO(OOCH)₂ · 2 H₂O). The Δν(COO⁻) values are quite comparable to that in sodium formate. It is difficult to distinguish between the ionic and the covalent chelate structure from these values, but it is expected of zirconium in its compounds to have bridging or bidentate formate groups so as to enable it to acquire coordination number as high as eight. Further evidence in this regard has been obtained by observing bands in the region below 700 cm⁻¹ which are not present in the spectrum of sodium formate, and therefore can be assigned to the Zr–O vibrations. On the other hand the absence of sharp intense bands in the region 900–1100 cm⁻¹ corresponding to discrete multiple bond Zr = O or a broad medium intensity band around 900 cm⁻¹ characteristic of infinite O–Zr–O–Zr–O–Zr chains containing bonds with multiple bond order indicate the absence of these species in these compounds¹⁴. The presence of narrow intense bands around 650 cm⁻¹, 480 cm⁻¹ and 350 cm⁻¹ may be assigned to the vibrations due to the Zr–O bonds. The band at 650 cm⁻¹ which is present only in the compound ZrO(OOCH)₂ · 2 H₂O may be assigned to the Zr=O vibration of the oxo group. Its slightly high value suggests the presence of a higher bond order Zr=O. The other bands at (485 cm⁻¹ and 350 cm⁻¹ for Zr(OOCH)₄ and 480 cm⁻¹ and 360 cm⁻¹ for ZrO(OOCH)₂ · 2 H₂O) may be assigned to the Zr–O single bond stretching vibrations arising due to the formation of bonds of Zr with oxygen atoms of the

### Table I. Some physical and analytical results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
<th>Molar conductance in Nitrobenzene</th>
<th>Analytical data**</th>
<th>Solubility***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OOCH)₄</td>
<td>d. 250</td>
<td>0.6</td>
<td>Zr [%] C [%] H [%]</td>
<td>i. C₆H₆, CCl₄, CHCl₃, CH₃Cl₂, CH₂CN, HCON(CH₂)₂, HCONH₂, H₂O s. C₆H₅NO₂, CH₂NO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>33.60 17.35 1.52</td>
<td>i. C₆H₆, CCl₄, CHCl₃, CH₃Cl₂, CH₂CN, HCON(CH₂)₂, HCONH₂, H₂O s. C₆H₅NO₂, CH₂NO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(33.63) (17.70) (1.47)</td>
<td>i. C₆H₆, CCl₄, CHCl₃, CH₂CN, HCON(CH₂)₂, HCONH₂, H₂O s. C₆H₅NO₂, CH₂NO₂</td>
</tr>
<tr>
<td>ZrO(OOCH)₂ · 2 H₂O</td>
<td>d. 250</td>
<td>0.4</td>
<td>39.01 10.40 2.42</td>
<td>s. HCONH₂, H₂O, C₆H₅NO₂, CH₂NO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(39.11) (10.29) (2.47)</td>
<td>s. HCONH₂, H₂O, C₆H₅NO₂, CH₂NO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39.01 10.40 2.42</td>
<td>s. HCONH₂, H₂O, C₆H₅NO₂, CH₂NO₂</td>
</tr>
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<td></td>
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<td></td>
<td>(39.11) (10.29) (2.47)</td>
<td>s. HCONH₂, H₂O, C₆H₅NO₂, CH₂NO₂</td>
</tr>
</tbody>
</table>

* cm² ohm⁻¹ mole⁻¹  
** Theoretical values are given in the parentheses.  
*** s = soluble, ss = slightly soluble, and i = insoluble.

### Table II. Infrared spectral bands (cm⁻¹) and their assignments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(O–H)</th>
<th>ν(COO⁻)</th>
<th>ν(COO⁻)</th>
<th>δ(O–H)</th>
<th>δ(OCO)</th>
<th>ν(Zr–O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOONa</td>
<td>—</td>
<td>1567 s</td>
<td>1366 s</td>
<td>—</td>
<td>772 m</td>
<td>—</td>
</tr>
<tr>
<td>Zr(OOCH)₄</td>
<td>—</td>
<td>1555 s</td>
<td>1360 s</td>
<td>—</td>
<td>760 m</td>
<td>450 m, 350 m</td>
</tr>
<tr>
<td>ZrO(OOCH)₂ · 2 H₂O</td>
<td>3350–3200 bs</td>
<td>1525 s</td>
<td>1345 s</td>
<td>1605 sh</td>
<td>755 m</td>
<td>650 s, 480 m, 360 m</td>
</tr>
</tbody>
</table>

bs = broad and strong, s = strong, m = medium, sh = shoulder.
A special feature of the infrared spectra of ZrO(OOCH)$_2$·2H$_2$O is the presence of a wide and strong absorption band at 3200–3350 cm$^{-1}$ which may be assigned to the stretching vibrations of the O–H bond. The displacement of this bond towards lower frequencies indicates that the water molecules are hydrogen bonded in the system. The spectrum also shows a band at 1605 cm$^{-1}$ which is assigned to HOH deformation.

Both compounds decompose fairly readily on heating but in stages. The thermogravimetric (T.G.) and differential thermogravimetric (D.T.G.) curves, have been plotted against temperature (°C). These curves for Zr(OOCH)$_4$ and ZrO(OOCH)$_2$·2H$_2$O are given in Fig. 1a and b, respectively. It is clear that at temperatures below 50 °C, these compounds do not undergo any change in weight. On further heating in the range 60–260 °C, tetraformatozirconium(IV) undergoes intensive decomposition accompanied by the liberation of volatile components and ZrO$_2$·H$_2$O is formed. The decrease in weight of 48.45% is observed (required weight loss for ZrO$_2$·H$_2$O/Zr(OOCH)$_4$ = 47.93%). Further increase in temperature leads to the formation of the final product, ZrO$_2$ which is complete at 450 °C corresponding to a weight loss of 54.50% (required weight loss for ZrO$_2$/Zr(OOCH)$_4$ = 54.57%). The thermal decomposition of tetraformatozirconium(IV) may thus be represented as:

\[
\text{Zr(OOCH)$_4$} \xrightarrow{60–260 \degree C} \text{ZrO$_2$·H$_2$O} \xrightarrow{260–450 \degree C} \text{ZrO$_2$}
\]

Diformatozirconium(IV) dihydrate loses two molecules of water up to 205 °C corresponding to a weight loss of 15.35% (required weight loss for ZrO(OOCH)$_2$/ZrO(OOCH)$_2$·2H$_2$O = 15.43%). On further heating it undergoes weight loss corresponding to the formation of an intermediate ZrO$_2$·H$_2$O. The observed weight loss is 40.05% (required weight loss for ZrO$_2$·H$_2$O/ZrO(OOCH)$_2$·2H$_2$O = 39.45%). The decomposition of the compound is complete at about 700 °C with the formation of ZrO$_2$. The thermal decomposition scheme may be summarized as:

\[
\text{ZrO(OOCH)$_2$·2H$_2$O} \xrightarrow{60–205 \degree C} \text{ZrO(OOCH)$_2$} \xrightarrow{305–340 \degree C} \text{ZrO$_2$} \xrightarrow{340–700 \degree C} \text{ZrO$_2$}
\]

The thermal decomposition of Zr(OOCH)$_4$ does not result in the formation of its oxoformate. This behaviour of the formate is very different from that observed for higher carboxylates of zirconium.$^{15}$

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**Fig. 1.** Thermal decomposition of

(a) Tetraformatozirconium(IV), Zr(OOCH)$_4$,

(b) Diformatozirconium(IV) dihydrate, ZrO(OOCH)$_2$·2H$_2$O.