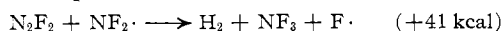


maximum. As shown in Figure 1, further addition of inert gas reduces the ratio  $\text{NF}_3:\text{N}_2$  and causes the appearance of unreacted  $\text{N}_2\text{F}_4$  in the products. This is the same phenomenon that we observed in the explosion of 1:1 mixtures of hydrogen:tetrafluorohydrazine and we explain it in the way we did before, namely, that reaction 3b is replaced by reaction 1 because the exothermic step

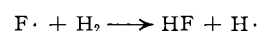
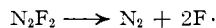


is replaced by the strongly exothermic step



When these mixtures are allowed to explode in the presence of large amounts of helium (>100 Torr), small but easily detectable amounts of difluorodiazine are found in the reaction products by gas chromatography. The finding of the diazine substantiates our hypothesis that it is an intermediate in the reaction and that its rate of disappearance decreases when large amounts of inert gas are present.

The question of whether these explosive reactions are thermal explosions or branching-chain explosions has not been brought up. It will be the subject of a future publication. In none of the chain-propagation mechanisms that we have proposed is there a step in which the number of radicals increases as is required by a branching-chain reaction. The fact that mixtures of hydrogen and difluorodiazine explode without being sensitized by tetrafluorohydrazine and the fact that difluorodiazine is capable of initiating free radical polymerization reactions are evidence<sup>7</sup> that the reactions



may occur and would provide a pathway for branching-chain explosions. The extent to which these steps occur has not yet been determined.

(7) C. Colburn, F. Johnson, A. Kennedy, K. McCollum, L. Metzger, and C. Parker, *J. Amer. Chem. Soc.*, **81**, 6397 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
MEMPHIS STATE UNIVERSITY, MEMPHIS, TENNESSEE 38111

## A Study of the Reactions of Zirconium(IV) Chloride with Some Aliphatic Acids<sup>1</sup>

BY J. LUDWIG<sup>2</sup> AND D. SCHWARTZ

Received September 24, 1969

The initial reaction of aliphatic acids with zirconium(IV) chloride at  $-15^\circ$  yields molecular addition compounds of the type  $\text{ZrCl}_4 \cdot 2\text{RCO}_2\text{H}$ . When heated to  $21^\circ$ , hydrogen chloride is eliminated and products are obtained which appear to have a composition represented by  $\text{ZrCl}_2(\text{RCO}_2)_2 \cdot 2\text{RCO}_2\text{H}$ . At temperatures over  $100^\circ$ , using an excess of the aliphatic acid,  $\text{Zr}(\text{RCO}_2)_4$  was obtained. Molecular weights of the tetrasubstituted products indicate monomer formation and a coordination number of 8 is suggested for zirconium.

### Introduction

The reaction of zirconium(IV) chloride with aliphatic acids has been studied by several investigators<sup>3-9</sup> and there is much disagreement among the various investigators and little, if any, information available in regard to infrared spectra, molecular weight data, and X-ray diffraction patterns of reaction products. Among the many reported reaction products are mono-, di-, tri-, and tetrasubstituted compounds as well as various compounds containing coordinated aliphatic

acid and hydrogen chloride. Also reported are hexacycloxydizirconium oxides and zirconyl derivatives as products from these reactions.

Some of the contradictory observations reported in the literature are undoubtedly due to the recognized complexity of the chemical behavior of zirconium. Many zirconium compounds have very little stability toward hydrolysis, and, therefore, difficulties are encountered in isolating and characterizing pure products. It is evident that the need for research in this area of zirconium chemistry is great. In view of this, an investigation of the reactions of zirconium(IV) chloride with acetic, propionic, *n*-butyric, and isobutyric acids was undertaken.

### Experimental Section

**Materials and Apparatus.**—The zirconium(IV) chloride was a commercial reactor-grade product from U. S. Industrial Chemical Co. Analysis of this material indicated 99.0%  $\text{ZrCl}_4$ . No appreciable improvement of purity was obtained on subliming the  $\text{ZrCl}_4$ . Thus, the commercial product was used as received, and

(1) Work done at North Dakota State University, Memphis State University, and the United States Steel Corp.

(2) Applied Research Laboratory, United States Steel Corp., Monroeville, Pa.

(3) W. B. Blumenthal, "The Chemical Behavior of Zirconium," Van Nostrand, 1958.

(4) L. W. Ryan and W. W. Plechner, *Ind. Eng. Chem.*, **26**, 909 (1934).

(5) R. M. Kapoor and R. C. Mehrotra, *J. Chem. Soc.*, 422 (1959).

(6) R. M. Kapoor and R. C. Mehrotra, *Chem. Ind. (London)*, 68 (1958).

(7) K. Sono, K. Hori, and C. Kajisoki, *Nagoya Kogyo Gijyutsu Shikensho Hokoku*, **5**, 142 (1956).

(8) R. M. Kapoor, K. C. Parde, and R. C. Mehrotra, *J. Indian Chem. Soc.*, **35**, 157 (1958).

(9) K. Z. Jaura and P. S. Bajura, *J. Sci. Ind. Res.*, **B**, **20**, 319 (1961).

TABLE I  
 ZIRCONIUM(IV) CHLORIDE-ACID ADDITION PRODUCTS

Product	%					
	Zr	Exptl Cl	Acid	Zr	Theoret Cl	Acid
ZrCl <sub>4</sub> ·2C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	24.60	36.00	40.32	23.93	37.21	38.86
ZrCl <sub>4</sub> ·2 <i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	23.30	34.05	44.09	22.29	34.65	43.06
ZrCl <sub>4</sub> ·2 <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	22.55	33.75	44.00	22.29	34.65	43.06

a glove box was used for all weighing and transferring. The organic acids and acid anhydrides which were used were reagent grade and were further purified by fractional distillation. All solvents were distilled over calcium hydride just prior to use.

All reactions were carried out in three-neck 500-ml round-bottom flasks. The flasks were fitted with a Teflon-covered magnetic stirring bar, a gas-inlet tube, a graduated dropping funnel, thermometer, and reflux condenser. All-glass apparatus with standard-taper, ground-glass interchangeable joints was used and special precautions were taken to exclude moisture. The reflux condenser was connected by glass tubing to a mercury bubbler, which in turn was connected to a water bubbler. A sintered-glass filter stick was used to disperse the gas in the water bubbler. Any hydrogen chloride evolved during the reactions was titrated with standard sodium hydroxide after being absorbed in the water bubbler. The mercury bubbler prevented any water vapor from entering the reaction flask. Before each reaction, the apparatus was thoroughly dried and purged with dry nitrogen. All transferring of reactants and products was accomplished in the dry nitrogen atmosphere of a glove box. Products were pressure filtered through sintered-glass filter funnels. The filtering process was also conducted in the glove box, using dry nitrogen as the pressurizing gas.

Fractionations of solvents and reactants were carried out in a 40-cm Vigreux column. The distillation apparatus was equipped for fractionating at reduced pressures.

**Preparation of Zirconium(IV) Chloride-Acid Adducts.**—Acetic, propionic, *n*-butyric, and isobutyric acids were allowed to react with ZrCl<sub>4</sub> in a mole ratio of 4:1 at reduced temperatures using carbon tetrachloride as the reaction medium. The reaction conditions for all four acids were the same.

In a typical experiment with propionic acid, 250 ml of CCl<sub>4</sub> and 38.35 g (0.1645 mol) of ZrCl<sub>4</sub> were placed in the 500-ml reaction flask. The flask was placed in a methanol-water Dry Ice bath and cooled to -15°. Carbon tetrachloride (75 ml) and 49.6 g (0.669 mol) of propionic acid were added dropwise from a dropping funnel to the ZrCl<sub>4</sub>-CCl<sub>4</sub> slurry with vigorous stirring. The resulting light yellow solution was maintained at -15° for 72 hr. During this time a white solid product precipitated without the evolution of any gaseous products. The solids were filtered, washed with cold carbon tetrachloride, and dried under reduced pressure. All of these operations were accomplished at approximately 0°. This was necessary to prevent the evolution of hydrogen chloride and the formation of substitution products.

Analysis of reaction products obtained from all of the reactions carried out with acid to ZrCl<sub>4</sub> ratios of 4:1 or more indicated a 2:1 adduct (see Table I). However, when the reactants were used in a mole ratio of 2:1, the product recovered had a much lower acid content.

At room temperature all of the adducts decomposed with the evolution of hydrogen chloride and the formation of substitution products. The adducts showed no permanent stability at -15°.

**Determination of Possible Substitution Products.**—Experiments were conducted in an attempt to determine the number of possible substitution products which might be obtained from the reaction of ZrCl<sub>4</sub> and acetic, propionic, *n*-butyric, and isobutyric acids.

ZrCl<sub>4</sub> was allowed to react with an excess of the various acids in an anhydrous solvent and the course of the reaction was followed by titrating the evolved hydrogen chloride with standard sodium hydroxide. In this way, by plotting the hydrogen chloride evolution *vs.* time, distinct breaks in the curve indicate mono-, di-, tri-, and tetrasubstitution products.

In a typical experiment using acetic acid, 28.46 g (0.1221 mol) of ZrCl<sub>4</sub> and 200 ml of dry xylene were placed in the 500-ml reaction flask. A solution of 50 ml of xylene and 60.10 g (1.008 mol) of acetic acid was placed in the dropping funnel. The ZrCl<sub>4</sub> to acetic acid ratio in this experiment was 1:8.25. The xylene-ZrCl<sub>4</sub> slurry was cooled to 0° and the xylene-acetic acid solution was added dropwise with vigorous stirring. A continuous nitrogen sweep was maintained through the system to carry any evolved HCl to the water bubbler. Standard sodium hydroxide solution was added through an opening in the top to neutralize the HCl as it was evolved. Phenolphthalein indicator was used in the water bubbler for the titration. The time and the amount of standard sodium hydroxide solution which had been added were recorded at frequent intervals.

At 0° no gas evolution occurred. The cooling bath was replaced with an oil bath and the reactor was heated slowly to 60°. A slow steady evolution of HCl occurred at this temperature. All solids dissolved leaving a clear solution; however, white solids began precipitating from the solution as the HCl evolution continued. The HCl evolution continued at 60-65° until 2 mol of HCl/mol of ZrCl<sub>4</sub> had been evolved. At this point the gas evolution ceased and an increase in temperature was necessary to continue the reaction. The temperature was increased slowly to 110°, at which temperature a slow but steady evolution of HCl occurred. This temperature was maintained until the HCl evolution ceased. At this point approximately 95% of the chlorine, which had been charged as ZrCl<sub>4</sub>, had been removed as HCl. The temperature was increased to 125° and the reaction mixture began refluxing. This temperature was maintained for several hours with very slow gas evolution. When no further gas evolution occurred, heating was stopped and the reaction was allowed to cool to room temperature.

This experiment was repeated with propionic, *n*-butyric, and isobutyric acids, using similar reaction conditions. It was necessary to use slightly higher reaction temperatures with these acids in order to maintain the HCl evolution. Experiments were conducted in which the acid to ZrCl<sub>4</sub> mole ratio was reduced to approximately 4:1. Other experiments were carried out in which a larger excess of acid was used in place of a solvent. Similar results were obtained in all of the reactions. The only difference among the various experiments was in the rate of HCl evolution. As the acid to ZrCl<sub>4</sub> ratio increased, the reaction time decreased. The plots of evolved HCl *vs.* time for all the experiments showed only the one distinguishable break at 2 mol of HCl/mol of ZrCl<sub>4</sub>.

**Preparation of the Dichlorodiacylates of Zirconium.**—Experiments were conducted using an acid to ZrCl<sub>4</sub> mole ratio of approximately 8:1 and reaction conditions identical with those described for the determination of possible substitution products. When 2 mol of HCl/mol of ZrCl<sub>4</sub> had been released, the reaction mixture was refrigerated at 0-5° for several days. The white solids which precipitated were filtered, washed with cold cyclohexane, and dried either under reduced pressure at room temperature or by passing dry nitrogen through them. In both cases the solids gradually turned to a paste-like resinous material. Attempts to dry the products at slightly elevated temperatures (35-40°) resulted in the evolution of HCl as the products gradually darkened to light brown.

Analyses of products dried at room temperature indicated a composition which can be represented by the formula ZrCl<sub>2</sub>·(RCO<sub>2</sub>)<sub>2</sub>·2RCO<sub>2</sub>H. In experiments in which the acids and ZrCl<sub>4</sub> were allowed to react in a mole ratio of 2:1, the evolution of hydrogen chloride ceased before 2 mol of HCl/mol of ZrCl<sub>4</sub>

has been released. White solid products from these reactions also rapidly turned to paste-like resinous material during attempts to dry them under reduced pressure.

**Preparation of the Tetraacylates of Zirconium.**—By allowing the acids to react with  $ZrCl_4$  in mole ratios of 4:1 or greater and at temperatures at which refluxing occurred, it was possible to remove 98–100% of the theoretical amount of HCl and subsequently to isolate the tetraacylates of zirconium.

In the case of acetic acid, the product was only slightly soluble in the xylene–acetic acid solution from which it was prepared even at the reflux temperature of 125°. The white solid product was filtered at room temperature, washed with dry cyclohexane, and dried under vacuum. Recrystallization of this product was accomplished from acetic anhydride.

In the case of propionic acid, no solid phase was present in the xylene–propionic acid solution at the reflux temperature of 140°. However, on cooling to room temperature, the white tetrapropionate precipitated rapidly. The product was recrystallized from propionic anhydride.

With both of the butyric acids considerable difficulty was encountered in isolating the pure tetrabutyrates. In those reactions in which hydrocarbon or halogenated hydrocarbon were used as solvents, clear amber solutions were obtained after the HCl evolution was completed. It was impossible to precipitate solids from these solutions either by cooling or by removal of solvent under pressure. In both cases solidification of the entire mixture eventually occurred. Pure products were obtained from reactions in which excess acid was used as the solvent. In a typical reaction, 51.73 g (0.222 mol) of  $ZrCl_4$  was allowed to react with 242 g (2.72 mol) of *n*-butyric acid. The reactor was heated slowly to maintain a steady evolution of HCl. When HCl evolution ceased, approximately 125 ml of butyric acid was removed from the clear amber solution by fractionation at 45° and 5 mm pressure. The white solid product could then be precipitated by storage at 3°. These products were recrystallized from solutions of the free acid.

**Analyses.**—Products were analyzed for zirconium, chlorine, and acyl content. Chlorine and acyl content were determined by weighing a sample directly into a glass-stoppered iodine flask. Standard sodium hydroxide solution was placed in the flared neck of the flask and added slowly by raising the glass stopper gradually. Any evolved gaseous hydrolysis products escaping from the flask were dissolved in the solution in the neck and thus were not lost. An excess of standard sodium hydroxide solution was used to hydrolyze the sample. After refluxing the mixture and filtering the hydrous zirconium oxide, the filtrate was divided into two equal parts. One part was analyzed for chlorine by the Volhard method. The second part was back-titrated with standard hydrochloric acid solution which gave the total acid content. The difference between the chloride analysis and the total acid content was taken as the acyl content of the sample. Zirconium content was determined by weighing samples directly into platinum crucibles. The samples were hydrolyzed with dilute ammonium hydroxide, dried in an oven at 110°, ignited at 1000° to constant weight, and weighed as zirconium dioxide. The dry nitrogen atmosphere of a glove box was utilized in all analytical procedures.

**Infrared Spectra.**—Infrared spectra were recorded on a Perkin-Elmer Model 421 double-beam spectrophotometer in the range 400–4000  $cm^{-1}$ . The potassium bromide disk technique was used but presented some problems. Clear disks could be readily prepared in the glove box; however, hydrolysis of the sample usually occurred as the spectra were being recorded.

The Nujol mull technique was also used with Nujol that was dried over calcium hydride, centrifuged, and then stored over calcium hydride. This technique gave better results than did the KBr-disk method, but occasionally some hydrolysis of the sample did occur.

The most satisfactory spectra were obtained from the products which were soluble in carbon tetrachloride. For these samples the complete exclusion of atmospheric moisture was possible with the use of sealed KBr cells.

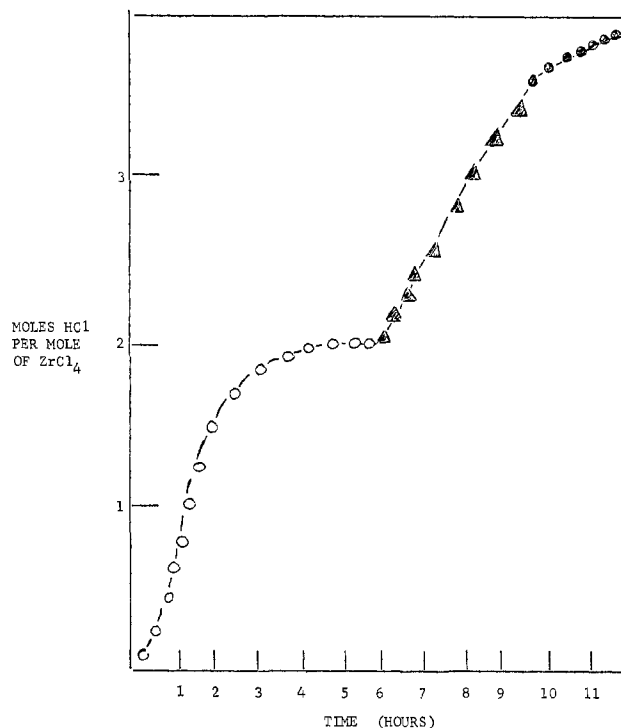


Figure 1.—Plot of time vs. evolution of hydrogen chloride for the reaction of zirconium(IV) chloride with acetic acid: O, 60–65°; ▲, 110°; ●, 125°.

**Molecular Weight Determinations.**—A Mechrolab Model 301A vapor pressure osmometer was used for the molecular weight studies. The instrument was calibrated with a concentration series of benzil in the various solvents which were used. The molecular weight determinations were also conducted in a glove box.

Because of limited solubility at room temperature, the molecular weight of zirconium(IV) acetate was not obtained. The molecular weight of zirconium(IV) propionate was determined in propionic acid. With the zirconium(IV) butyrates, molecular weights were obtained in the free acids and also in carbon tetrachloride. The molecular weights were determined over a concentration range of  $(0.7-11.0) \times 10^{-2} m$ .

**X-Ray Powder Data.**—A Norelco water-cooled unit of Type No. 12045 was used with a Philips Debye–Scherrer 114.59-mm camera using nickel-filtered copper  $K\alpha$  radiation. The relative intensities were determined with a Photovolt Corp. Model 52-C photometer which was equipped with a variable-response recorder. All samples were pulverized in the glove box and sealed in their glass capillaries to prevent hydrolysis.

## Results and Discussion

It appears likely that the initial reaction between  $ZrCl_4$  and a carboxylic acid would involve an initial addition product which could then liberate hydrogen chloride with the formation of substitution products.

Figure 1 shows a plot of time vs. evolution of hydrogen chloride for an experiment involving the reaction of  $ZrCl_4$  and acetic acid in a mole ratio of approximately 1:8 and using xylene as a solvent. It appears that hydrogen chloride evolution essentially stopped after 2 mol/mol of  $ZrCl_4$  has been released. This would indicate the probable formation of a disubstituted product. The results from experiments with propionic, *n*-butyric, and isobutyric acids, using the same reaction conditions, were similar to those for acetic acid.

TABLE II  
 ZIRCONIUM(IV) DICHLORODIACYLATES

Product	Exptl			Theoret		
	Zr	Cl	Acylate	Zr	Cl	Acylate
ZrCl <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> · 2CH <sub>3</sub> CO <sub>2</sub> H	23.06	17.32	60.19	22.79	17.71	59.50
ZrCl <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> · 2C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	18.99	14.89	67.32	19.99	15.54	64.47
ZrCl <sub>2</sub> ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>2</sub> · 2 <i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	16.90	12.65	70.25	17.80	13.84	68.36
ZrCl <sub>2</sub> ( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>2</sub> · 2 <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	15.20	10.80	74.75	17.80	13.84	68.36

 TABLE III  
 ZIRCONIUM(IV) TETRAACYLATES

Product	Exptl			Theoret		
	Zr	Cl	RCO <sub>2</sub>	Zr	Cl	RCO <sub>2</sub>
Zr(CH <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub>	28.15	0	72.20	27.86	0	72.14
Zr(C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>4</sub>	24.08	0	76.50	23.79	0	76.21
Zr( <i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>4</sub>	21.05	0	79.50	20.75	0	79.25
Zr( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>4</sub>	21.06	Trace	79.15	20.75	0	79.25

 TABLE IV  
 MOLECULAR WEIGHTS OF ZIRCONIUM(IV) BUTYRATES IN CARBON TETRACHLORIDE,  
*n*-BUTYRIC ACID, AND ISOBUTYRIC ACID

Zr( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>4</sub> <sup>a</sup>			Zr( <i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>4</sub> <sup>a</sup>		
Solvent	Concn, g/100 g of solvent	Mol wt	Solvent	Concn, g/100 g of solvent	Mol wt
CCl <sub>4</sub>	0.676	599	CCl <sub>4</sub>	0.767	589
	1.399	580		1.283	576
	2.169	554		2.081	523
	3.254	563		3.079	484
	4.914	528		4.256	463
<i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	0.595	462	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	0.525	457
	1.062	479		0.956	448
	1.987	470		1.413	506
	3.526	488		2.768	514
	4.734	479		3.999	484

<sup>a</sup> Calculated mol wt 439.6.

Table II contains the analytical data from those experiments which were designed to prepare the dichlorodiacylates of zirconium.

In analyzing the results obtained from these experiments, one should keep in mind the tendency of zirconium to attain the highest coordination number sterically possible by combination with electron donors. Thus, if the disubstituted molecule ZrCl<sub>2</sub>(RCO<sub>2</sub>)<sub>2</sub> is formed in the presence of excess acid, further coordination could occur with the free acid. The possibility of hydrogen bonding of the free acid to the zirconium compound also exists. In those experiments in which an initial ZrCl<sub>4</sub> to acid ratio of 1:2 was used, no free acid would be available for further coordination. The inability to remove the proper amount of HCl from these reaction mixtures might be explained by the formation of a coordinate link between the disubstituted zirconium compound and hydrogen chloride.

Table III contains the analytical results from the zirconium tetraacylates. All of these products were white crystalline solids which rapidly hydrolyzed in the presence of moist air. The acetate appeared to be the most sensitive to hydrolysis and the butyrates the least sensitive. Upon storage at room temperature in a dry nitrogen atmosphere for long periods of time (as long as 6 months), these products showed no signs of decomposition. The analyses and infrared spectra of the prod-

ucts after storage were identical with those obtained immediately after preparation. X-Ray powder photographs of the tetraacylates of zirconium were taken and all yielded very good diffraction patterns with clear, well-resolved lines.

It was not possible to obtain the molecular weight of zirconium(IV) acetate due to the very limited solubility at room temperature. However, the molecular weight of zirconium(IV) propionate was determined in propionic acid and the molecular weights of the butyrates were obtained in the corresponding free acids and also in carbon tetrachloride. The results of the molecular weight determinations are listed in Tables IV and V.

 TABLE V  
 MOLECULAR WEIGHTS OF ZIRCONIUM(IV)  
 PROPIONATE<sup>a</sup> IN PROPIONIC ACID

[Zr(C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>4</sub> ], g/100 g of C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	Mol wt	[Zr(C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>4</sub> ], g/100 g of C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	Mol wt
0.404	410	1.777	433
0.833	422	2.258	449
1.410	407		

<sup>a</sup> Calculated mol wt 383.5.

The results for the molecular weights of the butyrates in carbon tetrachloride show what appears to be an

abnormal phenomenon. The molecular weights appear to decrease with increasing concentration. However, this trend does not appear in the molecular weight determinations which were obtained in the free acids.

The molecular weight values for the tetraacylates in the corresponding acids show no significant variations with change in concentration. These values in the acid solvents more closely match those for the unassociated monomer than do those values which were obtained in carbon tetrachloride. Lower concentrations for determining the molecular weights could not be used due to the lack of sensitivity of the apparatus in the lower range and higher concentrations could not be used due to the limited solubility of the products. At the termination of the molecular weight experiments, the solvents were removed by evaporation at reduced pressure. X-Ray diffraction patterns of the recovered solids were identical with those of the original compounds.

The infrared spectra of zirconium tetraacetate and tetrapropionate were obtained using the KBr-disk and Nujol-mull techniques due to their limited solubilities in any suitable solvent. Using these methods some hydrolysis of the compounds did occur from atmospheric moisture as the spectra were being obtained. The spectra of the tetrabutyrates were obtained in carbon tetrachloride solution using sealed KBr cells. The absorption bands of the solvent were cancelled out by placing a second cell of the same thickness containing pure solvent in the reference beam.

The most interesting and important group of frequencies, from the point of view of interpreting the spectra, is the group due to the COO portion of the molecule. The spectra for all of the tetraacylates show a strong sharp absorption of  $1630\text{ cm}^{-1}$ . This corresponds to the antisymmetrical vibrations of the carboxyl group and, as would be expected, indicates a Zr-O bond of appreciable covalency. This peak at  $1630\text{ cm}^{-1}$  is very sharp and would indicate that all acylate groups around the zirconium are alike. In tetrakis(2,4-pentanedionato)zirconium, the  $1600\text{-cm}^{-1}$  band indicates a Zr-O bond of appreciable covalency resulting

from the coordination of the carbonyl oxygen to the zirconium.<sup>10</sup> Zirconium has a coordination number of 8 in this compound.

Several absorption bands occur in the tetraacylates which are not present in the free acids. These occur between  $1300$  and  $1450\text{ cm}^{-1}$ . This is the area in which many skeletal vibrations occur and it was not possible to make a position assignment for the symmetric carboxyl stretching frequency. The possibility exists therefore that the compounds have either structure I or II. Structure I would be favored due to it being



a less strained system while structure II would be favored by zirconium having its maximum coordination number of 8. Further evidence for structure II can be found by the examination of data from previous molecular weight studies of zirconium(IV) alkoxides and titanium(IV) dichlorodiacylates. Wardlaw, *et al.*,<sup>11</sup> have found that, except for the alcohols in which branching of the alkyl group causes steric hindrance, the zirconium alkoxides exist as polymers. They have also found that the molecular complexity is greater for the zirconium alkoxides than for the titanium(IV) alkoxides. This is probably due to the greater atomic radius of zirconium and its higher maximum coordination numbers. Molecular weight studies and infrared studies of titanium(IV) dichlorodiacylates<sup>12</sup> indicate that these compounds exist as dimers with the acylates acting as bridging groups between the titanium atoms. In light of the evidence of the tendency of zirconium to reach a coordination number higher than 4 (structure I) and the evidence presented here for the monomeric nature of the tetraacylates, structure II is a distinct possibility for the zirconium tetraacylates.

(10) "The Sadtler IR Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1967, Spectrum No. Y343K.

(11) W. J. Wardlaw, *J. Chem. Soc.*, 3569 (1955).

(12) D. Schwartz, C. Johnson, J. R. Ludwig, and M. L. Morris, *J. Inorg. Nucl. Chem.*, **26**, 2025 (1964).