TABLE IV

ACTIVITY COEFFICIENT OF NAPHTHALENE IN AQUEOUS SOLUTIONS OF ELECTROLYTES AT 0.1°

Electrolyte	Electrolyte concn., g.-eq./ liter	Optical density, $-\log (I/I_0)$, undiluted, at 25°, 275 mμ	Activity coefficient, $\gamma'' = s_0/s$	$\log \gamma''$
None	0	0.475 ± 0.004	(1.000)	(0.000)
¹/₂ Na₂SO₄	0.215	0.397	1.196	0.078
	.400	.342	1.389	.142
	.646	.278	1.708	.232
	.803	.240	1.978	.296
	1.071	.185	2.566	.409
	1.078	.197	2.410	.382
NaCl	0.345	.395	1.201	.080
	.537	.348	1.364	.135
	.689	.338	1.405	.147
	.896	.290	1.636	.214
	1.149	.257	1.846	.266
LiCl	0.275	.422	1.125	.051
	.371	.403	1.179	.071
	.550	.362	1.311	.118
	.743	.348	1.365	.135
	.917	.317	1.497	.175
	1.060	.298	1.593	.202
NaBr	0.293	.422	1.125	.051
	.515	.399	1.190	.076
	.735	.364	1.305	.116
	1.030	.315	1.508	.178
HCl	0.247	.458	1.037	.016
	.494	.450	1.055	.023
	.741	.431	1.102	.042
	.988	.419	1.134	.054

HCl and HClO₄, the absolute magnitudes of the salt effects are comparatively small and therefore subject to large relative error, which is compounded when one makes comparisons among the different non-electrolytes.

Data for naphthalene at 0.1° are presented in Table IV. Comparison of the Setchénow constants at the two temperatures, given in Table V, suggests no significant trend. Such differences as are apparent hardly exceed experimental error, and one

TABLE V

SETCHÉNOW CONSTANTS FOR NAPHTHALENE

Electrolyte	25°	0.1°
¹/₂ Na₂SO₄	0.358	0.366
NaCl	.260	.233
LiCl	.180	.191
NaBr	.169	.165
HCl	.046	.055

cannot establish a correlation with change in the water–electrolyte interaction, as suggested by the theory of McDevit and Long, though such a correlation apparently does exist for certain other non-polar non-electrolytes, and is not necessarily precluded by the present data.[5] An attempt was made to obtain data also for biphenyl at 0°, but the results were quite erratic; this is no doubt mainly due to the relatively large experimental error resulting from the low optical densities of the solutions, which were all below 0.300.

ENDICOTT, NEW YORK

Thermal Decomposition of MeCl₄·2C₆H₅COOR Type Compounds[1,2]

BY F. W. CHAPMAN, W. S. HUMMERS, S. Y. TYREE AND S. YOLLES

Zirconium tetrachloride-2-methyl benzoate, zirconium tetrachloride-2-ethyl benzoate and the analogous ester addition compounds of hafnium tetrachloride undergo thermal decomposition to yield alkyl chloride and metal benzoate. Superimposed on this reaction, free metal chloride reacts with metal benzoate to form benzoyl chloride and oxygen-bridge polymers. Indications are that pure hafnium addition compounds decompose at a slower rate than the corresponding zirconium compounds. Residues from decompositions that are carried to completion are resin-like solids insoluble in all common solvents except concentrated sulfuric acid.

It has been reported that thorium tetrabromide[3] and rare earth bromides[4] react with ethyl benzoate at the ester reflux temperature to evolve ethyl bromide and leave normal metal benzoates as insoluble residues. For two rare earths[4] differences in reaction rates indicated a separation factor. The possibility of a zirconium–hafnium separation factor using the same reaction was indicated. Preliminary experiments in this Laboratory showed that zirconium tetrabromide (and chloride) reacts with ethyl benzoate to produce ethyl bromide (chloride), but not in theoretical yield. Further-

more, zirconium tetrabenzoate was not the other product. Dangyan[5] has reported that iron(III) chloride refluxed with ethyl benzoate liberates ethyl chloride in no more than 74% yield. Norris and Klemka[6] prepared a product of composition AlCl₃·C₂H₅OOCC₆H₅ which decomposed slowly at 165° to liberate ethyl chloride in 95% yield. The composition of the solid residue was postulated as AlCl₂(OOCC₆H₅). In a previous paper[7] the authors reported the preparation of a series of addition compounds of the type MeCl₄·2C₆H₅COOR, (where Me = Hf or Zr, and R = ethyl, methyl or phenyl) all crystalline substances, stable at room temperature in dry air.

(1) From the doctoral dissertations of F. W. Chapman, W. S. Hummers and S. Yolles.

(2) Presented at the 119th Meeting of the A.C.S. at Cleveland, Ohio, April 11, 1951.

(3) R. C. Young, THIS JOURNAL, 56, 29 (1934).

(4) R. C. Young, A. Arch and W. V. Shyne, ibid., 63, 957 (1941).

(5) M. T. Dangyan, J. Gen. Chem. (U.S.S.R.), 8, 1780 (1938).

(6) J. F. Norris and A. J. Klemka, THIS JOURNAL, 62, 1432 (1940).

(7) W. S. Hummers, S. Y. Tyree and S. Yolles, ibid., 74, 139 (1952).

The results of studies on the pyrolysis of the following addition compounds are reported here: $ZrCl_4 \cdot 2C_2H_5OOCC_6H_5$, $ZrCl_4 \cdot 2CH_3OOCC_6H_5$, $HfCl_4 \cdot 2C_2H_5OOCC_6H_5$ and $HfCl_4 \cdot 2CH_3OOCC_6H_5$.

Experimental

The Thermal Decomposition of $ZrCl_4 \cdot 2C_2H_5OOCC_6H_5$.—Samples of the compound were thermally decomposed in an evacuated system with suitable provision to trap volatile products. At 125° a very slow rate of decomposition is indicated by the fact that whereas there is no change in the appearance, very little gas is evolved. The residue is soluble in water with the separation of an oil, typical of the behavior of the original substance. Analyses of the residue and the original substance indicate no appreciable change. At 150° the substance appears to melt slowly and, after an induction period, decomposes with the evolution of a gas, at the same time solidifying slowly. If the reaction is allowed to go to completion, the residue is a resin-like, light tan solid, insoluble in all common solvents except concentrated sulfuric acid. If the reaction is stopped during the gas evolution (by cooling) the residue obtained is partially soluble in water, zirconium and chloride being detected in the solution. At 175 and 200° identical results are observed although the rate of decomposition is much faster and the induction period is shortened. At 220-230° charring sets in. The gas evolved was identified as ethyl chloride with small, varying amounts of hydrogen chloride (1-5% by weight). The reaction is postulated as

$$ZrCl_4 \cdot 2C_2H_5OOCC_6H_5 \longrightarrow$$
$$ZrCl_2(OOCC_6H_5)_2 + 2C_2H_5Cl \uparrow \quad (1)$$
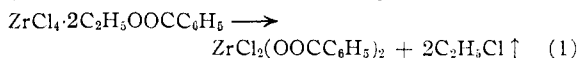
The amount of ethyl chloride evolved was determined by the weight of the gases trapped in ampoules with liquid air, correcting for the hydrogen chloride. The yield of ethyl chloride according to equation (1) was, in most trials, between 90 and 95%.

$ZrCl_4 \cdot 2C_2H_5OOCC_6H_5$ contains 17.35% Zr and 26.30% Cl. On heating a sample of the compound at 125° for six hours, a residue remained which contained 18.30% Zr and 25.90% Cl. A sample was heated at 150° until completely decomposed leaving a residue which contained 24.62% Zr and 18.60% Cl. The residue from a sample decomposed completely at 175° contained 25.14% Zr and 18.01% Cl. The residue from a sample decomposed completely at 200° contained 25.36% Zr and 17.80% Cl. The percentage composition of zirconium dibenzoate dichloride is 22.78% Zr and 17.50% Cl. It is apparent that equation (1) is not adequate to describe the reaction.

During decomposition runs drops of ethyl benzoate condensed on the inside walls of the system above the level of the thermostating liquid. The drops are believed to result from the dissociation of the addition compound.

$$ZrCl_4 \cdot 2C_2H_5OOCC_6H_5 \longrightarrow$$
$$ZrCl_4 + 2C_2H_5OOCC_6H_5 \uparrow \quad (2)$$
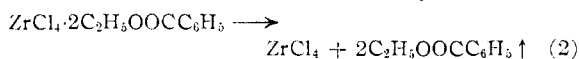
Attempts were made to measure the dissociation pressure in a differential manometer at temperatures below 100°. Discontinuous curves resulted when log p was plotted against $1/T$. Readings taken while increasing the temperature were not closely reproduced by readings taken while decreasing the temperature, an indication of irreversibility. It is probable that slight decomposition (of the sort reported at 125°) occurs below 100°.

Residues from decompositions carried out at 200° were found to contain small quantities of benzoyl chloride.

The Thermal Decomposition of $HfCl_4 \cdot 2C_2H_5OOCC_6H_5$.—Similar experiments were repeated with the hafnium compound with similar results. Again less than quantitative yields of ethyl chloride were obtained. $HfCl_4 \cdot 2C_2H_5OOCC_6H_5$ contains 28.32% Hf and 22.78% Cl. After heating a sample of the compound at 135° for eight hours a residue remained which contained 29.26% Hf and 22.24% Cl. The residue from a sample decomposed completely at 150° contained 39.70% Hf and 14.59% Cl. The residue from a sample decomposed completely at 175° contained 39.30% Hf and 15.40% Cl. For comparison, the calculated values for the postulated hafnium dibenzoate dichloride are 35.85% Hf and 14.53% Cl. A reaction similar to (1) is not adequate to describe the hafnium decomposition. Residues of hafnium compound decompositions at the higher tempera-

tures were found to contain small quantities of benzoyl chloride also.

The Preparation and Some Properties of $ZrCl_2(OOCC_6H_5)_2$ and $HfCl_2(OOCC_6H_5)_2$.—According to Jantsch[8] zirconium dibenzoate dichloride may be prepared by treating zirconium tetrachloride with benzoic acid in ether at the reflux temperature.

$$ZrCl_4 + 2HOOCC_6H_5 \longrightarrow$$
$$ZrCl_2(OOCC_6H_5)_2 + 2HCl \uparrow \quad (3)$$
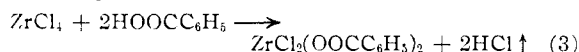
It was found that a pure product is difficult, if not impossible, to obtain by this method. This was not unexpected since Jantsch[8] prepared zirconium tetrabenzoate by the reaction of zirconium tetrachloride and benzoic acid in benzene at the reflux temperature.

$$ZrCl_4 + 4HOOCC_6H_5 \longrightarrow$$
$$Zr(OOCC_6H_5)_4 + 4HCl \uparrow \quad (4)$$
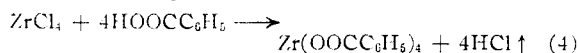
Jantsch proposed that all such substitutions proceed stepwise, and it is believed that a mixture of salts results the higher the temperature and the longer the reflux time the further the substitution proceeds toward the tetrabenzoate. At the ether reflux temperature a white crystalline product was obtained which contained 21.9% Zr and 17.5% Cl. The compound was heated in the thermal decomposition apparatus at 202° for four hours. A very small amount of white sublimate collected in the cold trap, but more volatile decomposition products were not detected. Qualitative tests showed the sublimate contained zirconium and chlorine. The extent of the decomposition was considered negligible. Apparently intramolecular reaction does not take place. Zirconium dibenzoate dichloride was mixed with excess zirconium tetrachloride and the mixture heated to 150°. No products volatile at this temperature were detected. Benzoyl chloride was identified in the residue by extraction with petroleum ether and preparing the p-toluidine derivative. The intermolecular reaction is postulated as

$$Cl_2Zr(OOCC_6H_5)_2 + ZrCl_4 \longrightarrow$$
$$Cl_2Zr\text{—}O\text{—}ZrCl_2OOCC_6H_5 + C_6H_5COCl \quad (5)$$
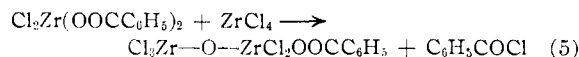
Zirconium dibenzoate dichloride was treated with excess ethyl benzoate at 200° with vigorous evolution of ethyl chloride. The residue contained 24.87% Zr and 6.71% Cl and was similar in appearance to the residues from the decomposition of zirconium tetrachloride-2-ethyl benzoate. Such a residue was treated with excess ethyl benzoate at 200°. Ethyl chloride was evolved. The residue was analyzed and contained 24.04% Zr and 6.78% Cl. Thus while not identical in composition, the decomposition residues undergo reactions similar to zirconium dibenzoate dichloride.

Identical experiments with hafnium compounds yielded substantially analogous results.

Reactions between Zirconium Tetrabromide and Ethyl Benzoate.—Zirconium tetrabromide and excess ethyl benzoate reacted at 190°. Ethyl bromide is evolved in 90% yield assuming a Young[8] decomposition.

$$ZrBr_4 + 4C_2H_5OOCC_6H_5 \longrightarrow$$
$$Zr(OOCC_6H_5)_4 + 4C_2H_5Br \uparrow$$
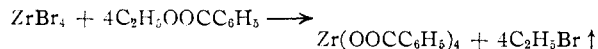
A petroleum ether extract of the residue was found to contain benzoyl bromide. The residue, after extraction, was insoluble in all common solvents except concentrated sulfuric acid and contained no bromine. The analysis corresponds most closely to a trimer, $Zr_3O_2B_8$, where B = $OOCC_6H_5$.

Calcd. for the compound: Zr, 21.45; Br, 0.00; C, 52.73; H, 3.16. Found for the residue: Zr, 21.91; Br, 0.00; C, 52.49; H, 3.45.

Zirconium tetrabromide and excess ethyl benzoate reacted at 170°. The results were similar but, in this case, the analysis of the residue after extraction to remove the benzoyl bromide, corresponds most closely to a dimer, Zr_2OB_6.

Calcd. for the compound: Zr, 19.72; Br, 0.00; C, 54.53; H, 3.27. Found for the residue: Zr, 20.17; Br, 1.12; C, 54.58; H, 3.38.

A similar reaction at 150° resulted in a residue which corresponds most closely to a dimer in which one bromine has not been replaced, Zr_2OB_5Br.

(8) G. Jantsch, *J. prakt. Chem.*, **115**, 7 (1927).

Calcd. for the compound: Zr, 20.64; Br, 9.04; C, 47.56; H, 2.85. Found for the residue: Zr, 21.75; Br, 8.69; C, 46.11; H, 2.57.

Discussion

The results reported are typical of the results of all thermal decompositions carried out. Analytical data on decomposition residues did not correspond to a simple dimer or trimer in all cases, but the data point overwhelmingly to polymerization. A reasonable mechanism for the reaction can be postulated. In the case of the addition compounds, a rather large proportion of the compound splits out ethyl chloride in accordance with equation (1), although the reaction probably proceeds stepwise. Jantsch[8] first proposed such a decomposition, but he found little evidence for such a reaction. However, Jantsch investigated mainly the reactions between zirconium tetrachloride and phenols, alcohols, carboxylic acids and β-diketones. A smaller amount of the addition compound dissociates according to (2), forming zirconium tetrachloride, which reacts with any zirconium benzoate salt linkage to start the polymerization. The extent of the polymerization depends probably upon the amount of free zirconium tetrachloride, which in turn must depend upon the temperature. Where excess ethyl benzoate is present it is possible (at least in the bromide case) to replace all halogen with benzoate *via* a reaction (1) mechanism.

The thermal decomposition of hafnium tetrachloride·2-ethyl benzoate, hafnium tetrachloride·2-methyl benzoate and zirconium tetrachloride·2-methyl benzoate resulted in data that are most easily interpreted according to similar mechanisms.

The original addition compounds are decomposed by water, in which the metal halide dissolves and the ester is liberated as an oil. The decomposition residues are insoluble in water. Appreciable differences between rates of decomposition of zirconium and hafnium compounds might effect a separation, even though the interaction of zirconium and hafnium compounds is indicated by the proposed mechanism of decomposition. The rate of evolution of ethyl chloride was used as a measure of the rate of decomposition. Such data permit a comparison of the rate of attack of alkyl benzoate upon zirconium–chlorine and hafnium–chlorine bonds, neglecting the equation (5) part of the reaction.

Experimental

Samples were thermally decomposed in a pyrolysis thimble attached to an evacuated system of known volume. Ampoules were sealed to the system in order that the volatile products might be collected for analysis. The pressure in the system was read using a Cromer diaphragm pressure transmitter.[9] Readings were reproducible to ±0.5 mm. Fig. 1 shows the results of several decomposition rate determinations. Curves 1, 2, 3 and 4 show the temperature effect on the rate of decomposition of zirconium tetrachloride·2-ethyl benzoate. Curves 5, 6 and 7 show the same for the corresponding hafnium compound. At 150° an appreciable difference in rate is observed between the zirconium and hafnium compounds. The Hf/Zr by weight in compounds used for curves 1, 2, 3 and 4 was 0.025.[10] The Zr/Hf in compounds used for curves 5, 6 and 7 were 0.022. A sample of hafnium oxide having a Zr/Hf of 0.0036 was used to prepare the compound in curve 8.
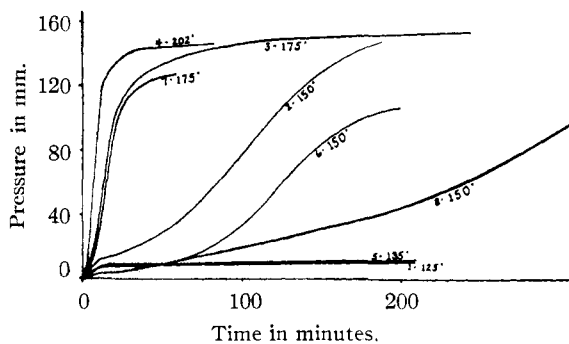

Fig. 1.

The rates of decomposition of methyl benzoate addition compounds were studied also. No decomposition of these compounds was observed at 150°, and the curves for rates of evolution of methyl chloride at 175° nearly coincide with those for rates of evolution of ethyl chloride at 150°.

A mixture of hafnium and zirconium tetrachloride·2-ethyl benzoate was decomposed partially, checking the extent of decomposition by the evolution of ethyl chloride. 2.66 g. of HfCl₄·2C₂H₆OOCC₆H₅ and 2.298 g. of ZrCl₄·2C₂H₆OOCC₆H₅ were mixed (Zr/Hf of mixture, 0.52), and subjected to thermal decomposition at 150° until the pressure in the system corresponded to one-half of the possible ethyl chloride. At this point the reaction thimble was chilled and the residue removed. As was true of all decompositions that were not carried to completion the residue was largely soluble in water; 1.9 g. of residue was extracted with water leaving an insoluble portion weighing 0.1196 g. The Zr/Hf in the insoluble portion was 1, although the precision of the spectroscopic determination of the ratio of Zr to Hf in this range is not high.[11] As expected from the data presented in Fig. 1, a partial separation of zirconium from hafnium was obtained, with a concentration of zirconium in the water-insoluble portion. The procedure does not however seem to offer a practical means of separation, since in order to obtain an enriched fraction the reaction must be stopped at such a point that too large a portion of the residue is soluble.

CHAPEL HILL, N. C.

(9) S. Cromer, U. S. A. E. C. Document No. MDDC-803.

(10) All Zr/Hf values determined at ORNL, Oak Ridge, Tennessee using the method of C. Feldman, *Anal. Chem.*, **21**, 1211 (1949).

(11) J. A. Norris, private communication.