and the two metals were determined in separate experiments and the heats of alloying were computed from those results, with no accounting being made for possible heats of mixing.

Biltz has criticized the work of Roos on the grounds that his heats of solution for the alloy and for the mixture referred to different final states. That criticism appears to be valid. As for Biltz's datum, calculations were made as if the alloy had a composition exactly 50.00%. If Biltz's alloy was of this composition, then the differences noted must be due to experimental error in both investigations, including Biltz's failure to account for heats of mixing. If, on the other hand, Biltz's alloy was of a composition nearly, but not exactly, equimolal, then that factor would enter also. An error of 0.01 in mole fraction would introduce an error of about 1800 cal./gram atom into the value reported.

In view of the known uncertainties there are probably no significant differences between the ΔH_f values determined calorimetrically and those obtained using the electrochemical cell. In three cases the calorimetric values are slightly higher, which is in the direction expected from the difference in order in the two cases. In the other case the difference is opposite to that expected. It is thus clear that the differences are too small in comparison with the uncertainties to permit an evaluation of the energies associated with the formation of magnesium–cadmium superstructures. About all that can be said is that the crude estimates based on theory appear to be high for the magnesium–cadmium system. The several theories of superstructures all indicate[17] an energy associated with the long range order of approximately $RT_c/2$, T_c being the order–disorder Curie temperature. On this basis the destruction of the several superlattices should alter the heats of formation of these alloys by roughly 300–500 cal. Differences of this magnitude should have showed up. Roos attempted to measure[16] the order–disorder transformation energy for MgCd by thermal analysis. His experiments gave a value of 140 cal./gram atom, which in view of the nature of this transformation and the method employed is probably somewhat low but may not be too far in error. The superstructures based on Mg_3Cd and $MgCd_3$ are less stable than that based on MgCd and undoubtedly have smaller energies of transformation. The magnitude of these energies makes the comparison of heats of formation a rather unattractive means for attempting their evaluation.

The failure of the heats of formation when plotted against composition to give a curve symmetrical about mole fraction 0.5 as required by the quasi-chemical theory has been referred to in II. There appears to be as yet no theory capable of explaining why the energy release accompanying the replacement of 25% cadmium with magnesium exceeds that of the converse process by a factor of two, or for that matter why the alloys are formed exothermally rather than endothermally. Such subleties of the alloying process appear to be for the moment solely within the province of the experimentalist.

(17) F. C. Nix and W. Shockley, *Rev. Mod. Phys.*, **10**, 1 (1938).

PITTSBURGH, PENNA. RECEIVED JUNE 27, 1951

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA IN CHAPEL HILL]

Compounds of Zirconium and Hafnium Tetrachlorides with Esters[1,2]

BY W. S. HUMMERS, S. Y. TYREE, JR., AND S. YOLLES

Zirconium tetrachloride·2-ethyl benzoate, zirconium tetrachloride·2-methyl benzoate, zirconium tetrachloride·2-phenyl benzoate, hafnium tetrachloride·2-methyl benzoate and hafnium tetrachloride·2-ethyl benzoate have been prepared and characterized. Heats of solution of hafnium tetrachloride, zirconium tetrachloride, methyl benzoate, ethyl benzoate, phenyl benzoate and the new compounds in nitrobenzene have been determined. The heats of formation of the new compounds have been determined.

It has been shown that certain rare earth tribromides react with ethyl benzoate to evolve ethyl bromide and leave insoluble rare earth tribenzoates.[3] Differences in the rate of these reactions for individual earths has been proposed as a basis of separation. Preliminary work in this Laboratory, aimed at establishing a separation factor for zirconium and hafnium, indicated that zirconium tetrahalides react with ethyl benzoate to yield ethyl halides, but that the residue is not zirconium tetrabenzoate. Furthermore, other decomposition products were identified, indicating that the reaction is not a well-defined double decomposition of the type proposed in the rare earth work. In an effort to delineate the nature of reactions between zirconium and hafnium tetrahalides and organic esters it was decided to isolate and characterize several molecular addition compounds first, and then study their decomposition.

The present paper describes techniques for the preparation of zirconium (and hafnium) tetrachloride–ester addition compounds and reports the determination of heats of formation of the compounds.

Experimental

The Preparation of Addition Compounds.—Rosenheim and Hertzmann[4] prepared zirconium tetrachloride·2-ethyl benzoate by refluxing an ether solution of zirconium tetrachloride and ethyl benzoate. Jantsch[5] repeated the preparation. In this Laboratory, Rosenheim's preparation was repeated successfully, but the yields were very low and the

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

(2) Presented at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April 11, 1951.

(3) Young, Arch and Shyne, THIS JOURNAL, **63**, 957 (1941).

(4) Rosenheim and Hertzmann, *Ber.*, **40**, 812 (1907).

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

products often impure. The reactions between metal halides and the esters were most conveniently carried out, with resulting purer products in liquid sulfur dioxide. A 500-ml. three-necked flask was fitted with a special dropping funnel, a Dry Ice–acetone condenser with a drying tube, a sintered glass filter stick and a magnetic stirrer. Anhydrous zirconium tetrachloride was loaded into the reaction flask in a dry-box. Dry sulfur dioxide was introduced through the side-arm in the dropping funnel and refluxed into the flask from the cold condenser finger until about 250 ml. of solvent had been added. The suspension was stirred while ethyl benzoate was introduced through the dropping funnel. A clear solution resulted, which was filtered through the sintered glass filter stick into a second flask identically equipped. The filtration was accomplished by closing the drying tube and forcing the solution into the second flask by the vapor pressure of sulfur dioxide. Upon evaporation to about 50 ml. of zirconium tetrachloride·2-ethyl benzoate crystallized. The delivery tube to the second flask was replaced with a dry filter stick, which was connected to a filter flask. The crystals were washed with three 50-ml. portions of dry benzene. The adhering solvent was removed by pumping at room temperature. The methyl benzoate addition compound was slightly soluble in sulfur dioxide resulting in a suspension. The addition compound was isolated from the first flask by filtration in this case thus eliminating the second flask. Table I lists the compounds prepared by this technique.

TABLE I[a]

Compound	Zirconium or hafnium, % Calcd.	Zirconium or hafnium, % Found	Chlorine, % Calcd.	Chlorine, % Found	Molecular weight Calcd.	Molecular weight Found
$ZrCl_4 \cdot 2(CH_3O_2CC_6H_5)$	18.23	18.51	28.01	27.66	506.4	509
$ZrCl_4 \cdot 2(C_2H_5O_2CC_6H_5)$	17.27	17.35	26.54	26.30	534.5	503
$ZrCl_4 \cdot 2(C_6H_5O_2CC_6H_5)$	14.64	14.86	22.49	22.88	630.6	604
$HfCl_4 \cdot 2(CH_3O_2CC_6H_5)$	29.71	30.02	24.08	23.86	589.8	551
$HfCl_4 \cdot 2(C_2H_5O_2CC_6H_5)$	28.36	28.32	22.98	22.78	617.2	618

[a] Molecular weights and percentage composition have been corrected for known zirconium–hafnium ratios.

Analysis.—The compounds were sampled in a dry-box and analyzed by standard gravimetric procedures for zirconium or hafnium and chloride. A comparison of the results with the calculated percentate compositions is given in Table I.

Molecular Weights.—Zirconium tetrachloride and hafnium tetrachloride and all addition compounds prepared were found to be moderately soluble in nitrobenzene and to exhibit no abnormalities in the concentration ranges used. Molecular weights were determined in nitrobenzene by the freezing point-lowering technique using a Beckmann thermometer, and by the vapor pressure-lowering method involving a differential manometer, using silicone 703 as the manometer fluid. The vapor pressure of purified solvent, nitrobenzene, checked the literature value. Values obtained are compared with calculated molecular weights in Table I.

Chemical Properties.—All of the addition compounds prepared are white crystalline powders. The substances are extremely hygroscopic and react with water instantaneously to dissolve the metal halide and separate the undecomposed ester as an oil or solid. On heating the compounds, decomposition (rather than melting) takes place, to yield ethyl chloride and polymeric residues. Also, on long standing some decomposition takes place. Analyses after several months show high values for hafnium and low values for chloride. The hafnium tetrachloride·2-ethyl benzoate is somewhat more soluble in liquid sulfur dioxide than the corresponding zirconium compound.

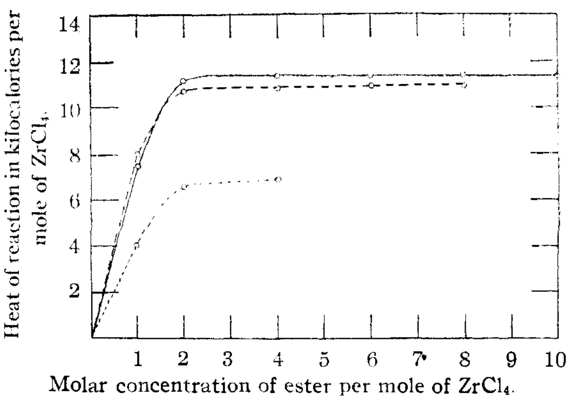

Fig. 1.—Heat of reaction of $ZrCl_4$ with esters at various ratios in nitrobenzene: — - — - — —, methyl benzoate; ———, ethyl benzoate; - - - - - - - - -, phenyl benzoate.

Thermochemical Data.—All heat measurements were made in a one-pint dewar flask, fitted with a large cork stopper, bored to accommodate a Beckmann thermometer, a propeller-type stirrer, an electric heater coil and a sample tube. The heating coil was #24 chromel wire wound in a spiral and enclosed in a U-shaped glass tube containing enough mineral oil to cover the spiral. Heater current was supplied from storage batteries and time measured with a stop watch.[6] The heat of solution of potassium nitrate measured with this calorimeter-checked literature values to within 1%. Heats of solution in nitrobenzene were determined for all compounds studied at concentrations from 0.01 to 0.1 molal. In this range the calculated molal integral heats of solution were plotted as a function of concentration, resulting in a straight line. Thus it may be concluded that (in the concentration range covered) the molal differential heats of solution are equal to the measured values, within the experimental error. All values reported are arithmetic means of determinations. Table II summarizes the heat of solution data.

TABLE II

HEATS OF SOLUTION IN NITROBENZENE IN KCAL./MOLE

Zirconium tetrachloride	10.5 ± 0.5
Hafnium tetrachloride	11.2 ± 0.4
Methyl benzoate	0.0
Ethyl benzoate	0.0
Phenyl benzoate	−5.7 ± 0.1
Zirconium tetrachloride·2-methyl benzoate	−6.4 ± .1
Zirconium tetrachloride·2-ethyl benzoate	−6.6 ± .3
Zirconium tetrachloride·2-phenyl benzoate	−3.3 ± .2
Hafnium tetrachloride·2-methyl benzoate	−2.3[a]
Hafnium tetrachloride·2-ethyl benzoate	−3.7[a]

[a] Average of only two determinations.

The same apparatus was used to measure the heat-change when pure ester was added to a solution of metal halide in nitrobenzene. In the zirconium series these heats of reaction were measured as a function of the ester–metal halide ratio. Table III shows the data for heats of reaction and Fig. 1 shows the effect of varying the mole ratio of ester to metal halide.

TABLE III[a]

$MeCl_4 \cdot xC_6H_5NO_2$	+ 2 ester →	Compound in solution + heat in kcal./mole
$ZrCl_4$	$C_2H_5OOCC_6H_5$	11.2
$ZrCl_4$	$CH_3OOCC_6H_5$	10.7
$ZrCl_4$	$C_6H_5OOCC_6H_5$	6.6
$HfCl_4$	$C_2H_5OOCC_6H_5$	10.8
$HfCl_4$	$CH_3OOCC_6H_5$	10.6

[a] Maximum standard error no greater than ±5%.

Discussion

Recapitulation of the thermochemical data as follows permits the calculation of the heat of formation of the compounds described in Table I.

First Set of Calculations

$$ZrCl_4(s) + XC_6H_5NO_2 \longrightarrow ZrCl_4 \cdot XC_6H_5NO_2 + 10.5 \text{ kcal.} \quad (1)$$

$$2(CH_3O_2CC_6H_5)(l) + XC_6H_5NO_2 \longrightarrow 2(CH_3O_2CC_6H_5) \cdot XC_6H_5NO_2 + 0.0 \text{ kcal.} \quad (2)$$

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[6] Daniels, Mathews and Williams, "Experimental Physical Chemistry," Third Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 109.

$$\mathrm{ZrCl_4{\cdot}2(CH_3O)_2CC_6H_5(s) + XC_6H_5NO_2 \longrightarrow ZrCl_4{\cdot}2(CH_3O_2CC_6H_5){\cdot}XC_6H_5NO_2 - 6.4\ kcal.} \quad (3)$$

$$\mathrm{ZrCl_4{\cdot}XC_6H_5NO_2 + 2(CH_3O_2CC_6H_5)(l) \longrightarrow ZrCl_4{\cdot}2(CH_3O_2CC_6H_5){\cdot}XC_6H_5NO_2 + 10.7\ kcal.} \quad (4)$$

Add (2) and (4) we obtain

$$\mathrm{ZrCl_4{\cdot}XC_6H_5NO_2 + 2(CH_3O_2CC_6H_5){\cdot}XC_6H_5NO_2 \longrightarrow ZrCl_4{\cdot}2(CH_3O_2CC_6H_5){\cdot}XC_6H_5NO_2 + XC_6H_5NO_2 + 10.7\ kcal.} \quad (5)$$

Add (3) to (5)

$$\mathrm{ZrCl_4{\cdot}XC_6H_5NO_2 + 2(CH_3O_2CC_6H_5){\cdot}XC_6H_5NO_2 \longrightarrow ZrCl_4{\cdot}2(CH_3O_2CC_6H_5)(s) + 17.1\ kcal.} \quad (6)$$

Then by adding (1), (2) and (6)

$$\mathrm{ZrCl_4(s) + 2(CH_3O_2CC_6H_5)(l) \longrightarrow ZrCl_4{\cdot}2(CH_3O_2CC_6H_5)(s) + 27.6\ kcal.}$$

A similar operation with the other compounds yields

$$\mathrm{ZrCl_4(s) + 2C_2H_5O_2CC_6H_5(l) \longrightarrow ZrCl_4{\cdot}2C_2H_5O_2CC_6H_5(s) + 28.3\ kcal./mole}$$

$$\mathrm{ZrCl_4(s) + 2C_6H_5O_2CC_6H_5(s) \longrightarrow ZrCl_4{\cdot}2C_6H_5O_2CC_6H_5(s) + 9.0\ kcal./mole}$$

$$\mathrm{HfCl_4(s) + 2C_2H_5O_2CC_6H_5(l) \longrightarrow HfCl_4{\cdot}2C_2H_5O_2CC_6H_5(s) + 25.7\ kcal./mole}$$

$$\mathrm{HfCl_4(s) + 2CH_3O_2CC_6H_5(l) \longrightarrow HfCl_4{\cdot}2CH_3O_2CC_6H_5(s) + 24.1\ kcal./mole}$$

Crude measurements of the heat of formation of zirconium tetrachloride·2-ethyl benzoate were made in the absence of any solvent, by adding a weighed quantity of zirconium tetrachloride to a measured proportion of ethyl benzoate. The values obtained were in agreement with those calculated from the solvent system measurements within ±2 kcal.

The points plotted in Fig. 1 are obtained by subtracting the heat of solution of ester from the gross heat measured. Thus these plots represent the heat effect of treating dissolved metal halide with dissolved ester without considering heats of dilution. The curves indicate compounds with ester–metal halide ratios greater than two to one are not stable under ordinary conditions. However, the slopes of the curves in the low ratio portions are such as to indicate the possibility of one to one addition compounds. There were indications that such compounds exist and a compound corresponding to a one to one addition was isolated when the reaction was carried out in a suspension of cyclohexane. However, the results were not reproducible.

Acknowledgment.—This investigation has been supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-234.

CHAPEL HILL, NORTH CAROLINA RECEIVED JUNE 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARPUR COLLEGE]

A Kinetic Salt Effect on the Acid-catalyzed Decomposition of Trioxane[1]

BY MARTIN A. PAUL

The rate of decomposition of trioxane into formaldehyde has been studied by a dilatometric method in solutions of perchloric acid and in solutions of perchloric acid mixed with sodium perchlorate at constant total ionic strength of 6 moles per liter, at 40°. At given perchloric acid concentration, the addition of sodium perchlorate markedly enhances the rate, an approximately sixfold increase being observed in 4 M $\mathrm{HClO_4}$ + 2 M $\mathrm{NaClO_4}$ as compared with 4 M $\mathrm{HClO_4}$. The effect may be closely correlated with a similar effect found by Harbottle on the acidity toward simple basic indicators. The rates in solutions of other strong acids may likewise be correlated with the indicator acidity function H_0 of Hammett and Deyrup, the first-order rate constant k (in $\mathrm{min.}^{-1}$) satisfying the empirical relationship: $\log k = -H_0 - 4.135$. These facts are consistent with the hypothesis that the rate-determining step consists of the slow rearrangement and decomposition of the acid ion conjugate to trioxane, which itself apparently functions as a simple weak base.

The author recently noted a correlation between the rate of decomposition of trioxane to formaldehyde in strongly acid solutions, measured by Walker and Chadwick, and the H_0 indicator acidity function of Hammett and Deyrup.[2-4] The reaction has now been followed in solutions containing perchloric acid and sodium perchlorate in varying proportions at fixed total electrolyte concentration of 6 moles per liter. The H_0 indicator acidity of such solutions has been established by Harbottle,[5] a quite marked progressive increase appearing in the acidity toward simple basic indicators of perchloric acid solutions as sodium perchlorate is added. Precisely the same effect is now reported on the rate of decomposition of trioxane.

Materials and Procedure.—Trioxane was obtained through the courtesy of the Electrochemicals Division, E. I. du Pont de Nemours and Co. It was recrystallized from water, and redissolved in water to form an approximately 2 M stock solution. Stock solutions of the various acids of approximately 8 M concentration (perchloric acid by dilution of Merck and Co., Inc., 70–72% reagent grade) were analyzed by titrating weighed samples against 0.2 M sodium hydroxide, standardized with National Bureau of Standards potassium hydrogen phthalate. Sodium perchlorate was the Eimer and Amend C.P. monohydrate.

A dilatometric procedure was used, similar to that described by Long and Purchase.[6] The dilatometer consisted simply of a glass bulb of about 60-ml. capacity, to which was attached a filling tube equipped with a stopcock, and a long open-ended capillary tube of about 1-mm. bore. In some of the dilatometers, a linear glass scale was affixed behind the capillary for determining the meniscus height. In others, the capillary tubes had linear scales engraved directly on them for greater convenience in reading and reduction of parallax error; these scales consisted of precision thermometer scales engraved by the Brooklyn Thermometer Co. on tubing previously selected for uniformity of bore. A droplet of mercury was placed above the solution meniscus to retard evaporation.

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(1) Presented before the Physical and Inorganic Chemistry Division of the American Chemical Society, Cleveland, Ohio, April, 1951.

(2) J. F. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, **39**, 974 (1947).

(3) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

(4) M. A. Paul, *ibid.*, **72**, 3813 (1950).

(5) G. Harbottle, *ibid.*, **73**, 4024 (1951).

(6) F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).