Silver Ion Complexes with 2-Thenylamine and 2-Furfurylamine[1]

By Ely Gonick, W. Conard Fernelius and Bodie E. Douglas

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The ability of 2-thenylamine and 2-furfurylamine to form complexes with metal ions has been investigated in an effort to establish whether or not the sulfur and oxygen atoms are active in coördination in these compounds.

Experimental

2-Thenylamine furnished by the Socony-Vacuum Oil Company was purified by distillation under nitrogen from barium oxide through a column packed with glass helices. The neutralization equivalent of the colorless fraction boiling at 78.5° (15 mm.) indicated a purity of 98.6%.

2-Furfurylamine furnished by the Quaker Oats Company and benzylamine purchased from Eastman Kodak Company were purified similarly by distillation from potassium hydroxide. The 2-furfurylamine boiled at 142.5–143° (735 mm.) and the benzylamine at 178° (742 mm.). The neutralization equivalents indicated purities of 99.9 and 99.7%, respectively.

Details of the experimental procedure are the same as those previously described.[2]

The terms used here and the method of calculation of constants are those given by Carlson, McReynolds and Verhoek.[3] The following constants were calculated.

Formation Constants of Silver–Ammines

Amine	log K_{AH}	log K_1	log K_2	log $K_{Av.}$
Benzylamine	9.46	3.02	3.78	3.40
2-Thenylamine	8.92	2.87	3.64	3.26
2-Furfurylamine	8.89	2.64	3.34	2.99

Since with all three amines $\bar{n}$ approaches a limiting value of two, it is evident that the S and O atom in 2-thenylamine and 2-furfurylamine, respectively, do not coördinate with silver ion which has a characteristic coördination number of two. The ions Cu^{++}, Ni^{++}, Co^{++} and Zn^{++} gave precipitates of hydroxides before there was any evidence of complex formation. Mercury(II) ion similarly gave a white precipitate containing organic material but with no well-defined stoichiometry.

2-Thenylamine and 2-furfurylamine resemble ammonia[4] and other amines[5] in the formation of silver ion complexes in that $\log K_1 < \log K_2$. Bruehlman and Verhoek[5] found that there was a direct proportionality between $\log K_1$ and pK_{AH} for the complexes of silver ion with primary amines, including benzylamine. 2-Thenylamine and 2-furfurylamine may now be included in this generalization.

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[1] Abstracted from a portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

[2] E. Gonick, W. C. Fernelius and B. E. Douglas, This Journal, **76**, 4671 (1954).

[3] C. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

[4] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[5] R. V. Bruehlman and F. H. Verhoek, This Journal, **70**, 1401 (1948).

Zirconium (and Hafnium) Tetrachloride·Diethyl Phthalate[1]

By R. V. Moore and S. Y. Tyree

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Addition compounds of zirconium tetrachloride and hafnium tetrachloride with esters of benzoic acid have been described in previous communications. The preparation and properties of addition compounds of the two tetrachlorides with an ester of phthalic acid are described in this paper.

Experimental

The Preparation of Addition Compounds.—The apparatus used has been described in a previous paper.[2] The same precautions must be taken to ensure anhydrous conditions. Five to 10 grams of metal tetrachloride is loaded into the reaction flask while in the dry-box. The apparatus is removed from the dry-box and 250 to 350 ml. of dry, liquid sulfur dioxide is condensed into the flask, entering through the side arm in a dropping funnel and refluxed from a Dry Ice–acetone cold finger. Diethyl phthalate is added from the dropping funnel. The solution clears abruptly when one mole of ester per mole of metal tetrachloride has been added. The solution is filtered into an identical flask through a filter stick under the vapor pressure of the solvent. The solution is allowed to evaporate to a volume of 25–50 ml. Some crystallization is noted usually at this point. Fifty to 75 ml. of cold benzene is added from a dropping funnel, which dissolves any crystalline material. A trapped aspirator pump is connected to the flask through a side arm on the dropping funnel, and the flask is evacuated. The flask is cooled externally while the pumping continues until the contents are frozen solid. Pumping is continued for 30 minutes to remove sulfur dioxide. When the flask is returned to atmospheric pressure and allowed to warm up, the white crystalline addition compound is slightly soluble in the benzene. The solvent is removed by suction through a filter stick and the product is washed with two 50-ml. portions of benzene, each of which is added through the dropping funnel and removed through the filter stick. The flask is left under vacuum overnight to remove the last traces of benzene. After the flask is placed in the dry-box the product is removed. No differences are observed between the zirconium and hafnium preparations. Yields from 75 to 80% are obtained. It is believed that the solubility of the product in benzene is the only reason for obtaining less than 100% yields. The solubility is much greater in benzene which contains sulfur dioxide.

Analysis.—The compounds were sampled in a dry-box and analyzed by standard gravimetric procedures for zirconium and hafnium and chloride. Molecular weights were determined in nitrobenzene by the freezing point lowering method using a Beckmann thermometer. In the zirconium compounds, Hf/Zr = 0.025 by weight. In the hafnium compounds, Zr/Hf = 0.022 by weight. Calcd. for $ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2$: Zr, 20.23; Cl, 31.08; mol. wt., 456. Found: Zr, 20.7; Cl, 31.5; mol. wt., 471. Calcd. for $HfCl_4 \cdot C_6H_4(COOC_2H_5)_2$: Hf, 32.47; Cl, 26.31; mol. wt., 539. Found: Hf, 33.2; Cl, 25.6; mol. wt., 610.

Chemical Properties.—The addition compounds are white, freely flowing crystalline substances. They are stable in dry air. When added to water the compounds decompose, with the metal halide dissolving in the water and the ester separating as an oil. No melting points are observed for the compounds. They decompose on heating, although while decomposing they go through a liquid stage.

Thermochemical Data.—All heat measurements were made in the apparatus described previously.[3] The heats of solution of diethyl phthalate and the hafnium addition compound in nitrobenzene are too small to measure with the apparatus used. A plot of the integral heat of solution of the zirconium addition compound in nitrobenzene against the concentration from 0.025 to 0.112 molal gives a line that is slightly concave, but does not deviate too much from a straight line. The molal heat of solution at 0.1 molal dilution is 2.3 kcal./mole. Bulbs of anhydrous metal halide

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[1] From the doctoral dissertation of R. V. Moore.

[2] W. S. Hummers, S. Y. Tyree and S. Yolles, This Journal, **74**, 139 (1952).

were broken under nitrobenzene solutions of the ester in the calorimeter. The arithmetic mean of five determinations for the heat of the reaction between zirconium tetrachloride and the ester–nitrobenzene solution is −15.9 kcal./mole of metal chloride. The corresponding value for the hafnium reaction is −17.6 kcal./mole of metal chloride. The standard error in these determinations was 5%.

Taking the values for the integral heats of solution of zirconium tetrachloride and hafnium tetrachloride in nitrobenzene at 0.1 molal dilutions as −10.5 and −11.2 kcal./mole, respectively, it is possible to calculate the heats of formation of the addition compounds from the ester and the metal chloride as

$$\mathrm{ZrCl_4(s)} + x\mathrm{C_6H_5NO_2} \longrightarrow \mathrm{ZrCl_4 \cdot }x\mathrm{C_6H_5NO_2} + 10.5\ \mathrm{kcal.} \quad (1)$$

$$\mathrm{C_6H_4(COOC_2H_5)_2(l)} + x\mathrm{C_6H_5NO_2} \longrightarrow \mathrm{C_6H_4(COOC_2H_5)_2 \cdot }x\mathrm{C_6H_5NO_2} + 0.0\ \mathrm{kcal.} \quad (2)$$

$$\mathrm{ZrCl_4(s)} + \mathrm{C_6H_4(COOC_2H_5)_2 \cdot }x\mathrm{C_6H_5NO_2} \longrightarrow \mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2 \cdot }x\mathrm{C_6H_5NO_2} + 15.9\ \mathrm{kcal.} \quad (3)$$

$$(2) + (3)\ \mathrm{ZrCl_4(s)} + \mathrm{C_6H_4(COOC_2H_5)_2(l)} + x\mathrm{C_6H_5NO_2} \longrightarrow \mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2 \cdot }x\mathrm{C_6H_5NO_2} + 15.9\ \mathrm{kcal.}$$

$$\mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2(s)} + x\mathrm{C_6H_5NO_2} \longrightarrow \mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2 \cdot }x\mathrm{C_6H_5NO_2} - 2.3\ \mathrm{kcal.} \quad (4)$$

$$(2) + (3) - (4)\ \mathrm{ZrCl_4(s)} + \mathrm{C_6H_4(COOC_2H_5)_2(l)} \longrightarrow \mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2(s)} + 18.2\ \mathrm{kcal.}$$

Similar operations with the hafnium data give

$$\mathrm{HfCl_4(s)} + \mathrm{C_6H_4(COOC_2H_5)_2(l)} \longrightarrow \mathrm{HfCl_4 \cdot C_6H_4(COOC_2H_5)_2(s)} + 17.6\ \mathrm{kcal.} \quad (5)$$

The values are significantly less than the corresponding values for the two to one benzoate addition compounds, excepting the phenyl benzoate case. It is inferred from the thermochemical experiments that only one addition compound of the ester and the metal halide exists, since above a 1:1 mole ratio of ester to metal chloride, the heat of reaction is independent of the ratio.

The Thermal Decomposition of the Addition Compounds.—The compounds decompose to give gaseous products and a non-volatile residue, as is observed with the zirconium tetrachloride and hafnium tetrachloride benzoate addition compounds.[4] Below 150° the decomposition of the diethyl phthalate addition compounds is very slow in dry air or in a vacuum. At 150° they are decomposed completely in six hours, and the zirconium compound decomposes more rapidly than the hafnium compound. At 160° both decompose completely in about three hours. At 180° the decomposition is more vigorous still, and the compounds melt while decomposing. There is considerable frothing of the liquid. In about 20–30 minutes the decomposition is substantially complete and the residue is a brown solid. Rates of decomposition were measured by following the increase in pressure within a closed system containing the compounds. The rate curves are of the same general shape as those reported for the benzoate addition compounds.[3]

The gaseous products of decomposition were subject to infrared scanning using a Beckman Model IR-2 recording spectrophotometer. Chemical tests identified ethylene, hydrogen chloride and sulfur dioxide in the gaseous mixture. The apparent molecular weight of the mixture of gaseous products from a number of decomposition runs was determined. The average was 57, with individual results varying from 55 to 59.

The solid decomposition residue is insoluble in all common solvents. In hydrochloric and nitric acids, some of the solid dissolves, but there is always a residue insoluble even on long digestion. The composition of the residue varies from run to run. Values range from 25.7 to 29.7% Zr and from 17.9 to 21.4% Cl with averages at 29.1% Zr and 19.9% Cl in the zirconium case. Values range from 42.3 to 44.4% Hf and from 11.2 to 15.9% Cl with averages at 43.4% Hf and 14.1% Cl in the hafnium case.

Discussion

The diethyl phthalate addition compounds are difficult to isolate in a high state of purity. The analytical values are averages of a number of determinations on samples prepared at different times. The compounds are similar to the benzoate ester addition compounds in most respects. As might be expected the mole ratio of ester to metal halide is 1:1 rather than the 2:1 found in the case of the monofunctional esters.

It is apparent that the zirconium addition compound contains about 4 mole % excess zirconium tetrachloride, whereas the hafnium addition compound contains less than the calculated percentage of chlorine. The heat of solution of zirconium tetrachloride in nitrobenzene is not large enough to account for the apparent difference between the heats of solution of the two addition compounds. Furthermore, correcting for the excess zirconium tetrachloride increases the difference, inasmuch as the solution of zirconium tetrachloride in nitrobenzene is an exothermal process. The Cl/Zr ratio of the zirconium compound is 3.96, whereas the Cl/Hf ratio is 3.80. The latter value may be the result of some reaction between the ester and the tetrachloride at room temperature. It is difficult to see how a slight amount of decomposition can account for the observed differences in heat of solution values.

The infrared absorption spectra of the decomposition gases showed clearly the presence of ethyl chloride, ethylene, hydrogen chloride and sulfur dioxide, the last three being present in small quantities. The sulfur dioxide is present as an impurity from the preparative technique and could not be removed by prolonged pumping. It was estimated from a number of the infrared absorption traces that the decomposition gases contained on the average about 2% ethylene. Quantitative measures of the amount of hydrogen chloride present in the gases were made by direct titration. They showed much variation from run to run. This is expected since traces of moisture react with the original addition compounds to produce hydrogen chloride. When the apparent molecular weights of samples of the gases are corrected for the estimated ethylene and hydrogen chloride present, the values approach the molecular weight of ethyl chloride. The most acceptable value for the equilibrium constant $K_p = \dfrac{P_{\mathrm{C_2H_5Cl}}}{P_{\mathrm{C_2H_4 \cdot HCl}}}$ is 780 mm.$^{-1}$ at 180°, calculated from the equation of Lane, Linnett and Oswin.[4] With such a value, it is unlikely that the amount of ethylene present in the decomposition gases could arise from the dissociation of ethyl chloride.

The primary decomposition mechanism that satisfies most of the observations is represented by equation 6.

$$\mathrm{ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2} \longrightarrow \mathrm{ZrCl_2(OOC)_2C_6H_4} + 2\mathrm{C_2H_5Cl} \quad (6)$$

The total pressure of decomposition gases observed in a system of known volume approximated that calculated according to equation 6 in all cases. The calculated composition of zirconium dichloride phthalate is 28.20% Zr and 21.66% Cl. The results of analyses of actual residues scatter around these values. The same is true for the hafnium residues. It is certain that the decomposition does

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(3) F. W. Chapman, W. S. Hummers, S. Y. Tyree and S. Yolles, THIS JOURNAL, **74**, 5277 (1952).

(4) M. R. Lane, J. W. Linnett and H. G. Oswin, *Proc. Roy. Soc. (London)*, **216A**, 361 (1953).

not proceed by the primary mechanism alone. Drops of diethyl phthalate have been identified in the decomposition apparatus, which suggests dissociation according to equation 7

$$ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2 \longrightarrow ZrCl_4 + C_6H_4(COOC_2H_5)_2 \tag{7}$$

It is possible that the ethylene results from the decomposition of the ester, as reported for ethyl benzoate.[5] If this is so, the phthalic acid, resulting from equation 8, would react with any free metal tetrachloride to give hydrogen chloride.

$$C_6H_4(COOC_2H_5)_2 \longrightarrow C_6H_4(COOH)_2 + C_2H_4 \tag{8}$$

$$ZrCl_4 + C_6H_4(COOH)_2 \longrightarrow ZrCl_2(OOC)_2C_6H_4 + 2HCl \tag{9}$$

In the zirconium case only, trace quantities of phthalic anhydride were identified among the decomposition products.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-234.

[5] E. M. Bilger and H. Hibbert, THIS JOURNAL, **58**, 823 (1936).

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Henry's Law Constants for *t*-Butyl Chloride in Aqueous Methanol Solutions[1]

BY A. R. OLSON, W. C. RUEBSAMEN AND W. E. CLIFFORD

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Rate equations proposed by various investigators for the solvolysis of *t*-butyl chloride in aqueous methanol solutions involve Henry's law constants for *t*-butyl chloride in those solvents.[2-4] The original determinations of these constants by Halford[5] as quoted by Olson and Halford, admittedly were subject to appreciable errors. We have therefore redetermined the constants as a contribution to the program of limiting the form of the rate equation.

Experimental Part

Two methods were used. In the first method a series of Liebig bulbs, containing *t*-butyl chloride in the solvent under consideration, were connected in series and placed in a thermostat. A known volume of nitrogen was then passed through the bulbs and collected in a large bulb. The bulb was cooled, some water admitted to it, and then sealed. It was then warmed to hydrolyze the chloride, and the resulting acid was titrated. The concentration of the chloride in the last Liebig bulb likewise was determined by completely hydrolyzing a known volume of the solution. In the 100 and 90% methanol solutions, three bulbs were sufficient to saturate the nitrogen so that the composition of the last bulb remained unchanged, but in the 80 and 70% solutions, eight bulbs were needed. No spray could be detected when the effluent gas was admitted to the chamber of an ultra-microscope.

From the known empirical rate equation, the time of mixing and the initial and final times of passage of the gas, an average concentration for the chloride was calculated, *i.e.*

$$N_{av} = N_0 \left[\frac{1 - \frac{k}{2}\left\{(t_f - t_0)^2 - (t_i - t_0)^2\right\}}{t_f - t_i} \right]$$

This correction amounted to about 4% in the 70% methanol and to only about 1% in the 80% methanol.

Duplicate runs were made using pure *t*-butyl chloride in the Liebig bulbs. From these data the vapor pressure of pure *t*-butyl chloride at 25° was determined to be 300 mm. A check on this value was found by the following static method. Freshly distilled *t*-butyl chloride was introduced into a flask which was fitted to a manometer and a vacuum line. The liquid was frozen, the system evacuated, and then the liquid was permitted to warm up. This degassing procedure was repeated several times. With the bulb kept somewhat below room temperature, the equilibrium pressure was read. Now a series of seven determinations in a temperature range slightly below room temperature were made, and from the normal boiling point, 50.7°, the equation

$$\ln p = 17.40 - \frac{3487}{T}$$

was found to fit with an average deviation of 0.2%. This agrees with the dynamic determination at 25°. ΔS of vaporization is normal for a non-associated liquid.

The second method was essentially a repetition of Halford's method with some experimental improvements, *e.g.*, the volume of the vapor space was reduced to about 30 ml., a magnetic stirrer was introduced to speed equilibrium, and mercury was interposed between the *t*-butyl chloride and the stopcock.

Results

At 25° the constants obtained by the static method agreed with those obtained by the dynamic method for the 100 and 90% methanol solutions, but slightly lower values were obtained in the more aqueous solvents. Since correction had been applied for the change in concentration because of evaporation and the change due to the change in mole fraction, the most likely cause of error was thought to be the solvolytic reaction; and so the temperature was reduced to 0°. At this temperature, pressures remained constant for long times. In the higher water solvents a pronounced cooling was noticed on the addition of the *t*-butyl chloride.

Plots of log $(p/N)_{BuCl}$ *vs.* volume per cent. of water in the solvent are practically straight lines for both sets of data. If the point for pure methanol at 0° is superimposed on the point for pure methanol at 25°, a rotation of about 3.5° makes the two curves coincide. This permits an easy and precise extrapolation of the 25° curve.

The steeper slope of log (p/N) *vs.* volume per cent. of water for the 0° data is consistent with the cooling mentioned above, for

$$\frac{\partial \log (p/N)_{BuCl}}{\partial T} = \frac{H^* - \bar{H}}{RT^2}$$

Since $H^* - \bar{H}$ decreases as the water content increases and since H^* is constant, $\bar{H}$ must increase.

The results are collected in the Table I.

TABLE I

Methanol, vol. %	log P/N	t, °C.	Methanol, vol. %	log P/N	t, °C.
100	3.350	25	100	2.634	0[a]
90.17	3.697	25	70.5	3.951[b]	0
80.09	4.043	25	60.5	4.292	0
70.45	4.390	25	49.5	4.723	0

[a] We are indebted to Mr. Hultgren of this Laboratory for making the measurements at 0°. [b] Probably several per cent. high. Neglected in drawing line.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[2] A. R. Olson and R. Halford, THIS JOURNAL, **59**, 2644 (1937).

[3] P. Bartlett, *ibid.*, **61**, 1630 (1939).

[4] S. Winstein, *ibid.*, **61**, 1635 (1939).

[5] R. Halford, Ph.D. thesis, University of California, Berkeley, 1938.