must be close to $[ZrO_2]_n$. However, the crystalline hydrous zirconias still contain significant amounts of coordinated water and hydroxyl groups as shown by their high ignition loss ($\sim$11% when dried over P_2O_5) and retention of ion-exchange properties.[11] These groups must be primarily located on the surface of the crystallites. Thus, the crystalline, hydrous zirconias are considered to be hydrated oxo-hydroxides.

The results reported here lend substance to Lundgren's observation. In a subsequent publication the structure of the various forms of hydrous zirconia will be discussed in more detail and their relationship to the aqueous Zr(IV) species developed.

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Molecular Addition Compounds of Tin(IV) Chloride. III. Thermodynamic Data for 1:1 Addition Compound Formation[1]

BY JAAN LAANE AND THEODORE L. BROWN[2]

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In an earlier study of the equilibria existing between benzonitrile and tin(IV) chlorides, it was observed that the 1:1 addition compound is the principal complex species present in dilute benzene solution, although formation of a 1:2 addition compound, $SnCl_4B_2$, was found to occur to a measurable extent.[3] We wish to report here some further observations on benzonitrile–tin(IV) chloride complexes, as well as data relating to the interaction of tin(IV) chloride with a few oxygen donors. Equilibrium constants have been evaluated as a function of a temperature to permit calculation of the enthalpy and entropy of complex formation.

Experimental

The substances employed as donors were obtained commercially and purified by drying and distillation or sublimation before use. Reagent grade tin(IV) chloride was fractionated over mercury before use. Reagent grade benzene was dried using sodium wire. All operations in the preparation and handling of solutions were conducted in a drybox.

Measurements were carried out with a Beckman IR-7 spectrophotometer using cells with sodium chloride windows, 0.4-mm. path length. The temperature was controlled to within about 0.2° by placing the cells in a box fitted with sodium chloride windows. Air, pre-heated or pre-cooled as required, is passed into the chamber. The temperature in the chamber is controlled by a thermistor element which controls the operation of a heater in the incoming air stream. The procedures involved in the determination of the equilibrium constants are essentially the same as those described earlier. In the present work the interest is in evaluation of only K_{11}, since it was concluded that K_{12} could not easily be evaluated with sufficient accuracy to be of use in estimating an enthalpy for 1:2 compound formation. In the case of the nitriles the concentration conditions imposed by the extinction coefficient of the nitrile band are such that a significant quantity of 1:2 compound formation occurs. The iterative technique described previously[3] was therefore employed in calculating K_{11}.

Addition compound formation in the carbonyl donor systems was measured by observation of the infrared carbonyl absorption. The carbonyl absorption for complexed molecules is shifted to lower frequency; the frequency shift is sufficiently large (Table I) so that the correction for overlap with the free carbonyl absorption is small. The extinction coefficients for the carbonyl bands are much higher than for the nitriles, and it was possible to achieve conditions under which formation of the 1:2 complex is negligible. K_{11} for the carbonyl donor systems was calculated, therefore, from the expression

$$K_{11} = \frac{B_0 - B}{B(A_0 - B_0 + B)}$$

where A_0 and B_0 represent the initial concentrations of tin(IV) chloride and carbonyl compound, respectively, and B represents the equilibrium concentration of free carbonyl compound, as determined from the infrared measurement. Preliminary studies revealed that K_{12} is smaller than K_{11}; by employing excess tin(IV) chloride to minimize formation of the 1:2 adduct, essentially constant values were obtained for K_{11} under varying concentration conditions.

Results

The results of the measurements are given in Tables I and II, along with values of ΔH and ΔS calculated from the $1/T$ dependence of log K. Each value listed for K is the result of measurements on a number of solutions, in which both donor and acid concentrations are varied over a tenfold range. The standard deviations in the values of K_{11} are in all cases about 0.2 or less. The uncertainty in the values of ΔH are estimated from the log K *vs.* $1/T$ graphs and the standard deviations for the values of log K. The uncertainty in ΔS is due largely to the uncertainty in the value of ΔH.

TABLE I

CARBONYL FREQUENCY DATA IN CARBONYL–TIN(IV) CHLORIDE BENZENE SOLUTIONS

Donor	ν_{free}	ν_{complex}	$\Delta\nu$
Diisobutyl ketone	1712	1642	70
9-Fluorenone	1720	1666	54
Ethyl pivalate	1728	1646	82

It is to be noted that although the values listed for K are in units of l./mole, the values of ΔS were calculated[4] using K in units of atm.$^{-1}$.

Discussion

A graph of ΔH *vs.* ΔS for the five benzene solution systems listed in Table II is shown in Fig. 1. Linear enthalpy–entropy relationships such as that in Fig. 1 have been discussed recently by Person.[5] It is interesting that a linear relationship does in fact hold for

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(1) Address correspondence regarding this note to T. L. Brown. This research was supported by a PHS research grant, A-3551, from the Institute of Arthritis and Metabolic Diseases.

(2) Alfred P. Sloan Foundation Fellow.

(3) T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 331 (1961).

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, Calif., 1960, pp. 348–349.

(5) W. B. Person, *J. Am. Chem. Soc.*, **84**, 536 (1962).

TABLE II

EQUILIBRIUM CONSTANTS FOR 1:1 ADDITION COMPOUNDS WITH TIN(IV) CHLORIDE IN BENZENE SOLUTION

Donor	K_{11}, l./mole	ΔH, kcal./mole	ΔS,[a] cal./°K. mole
p-Chlorobenzonitrile	4.3 (20°); 3.6 (25°); 2.9 (30°); 2.2 (35°)	-7.1 ± 0.5	-15.0 ± 1.5
(in, 1,2-dichloroethane)	K_{11} at 30°, 2.9; K_{12} at 30°, 1.6	....	....
p-Methoxybenzonitrile	15.5 (30°); 10.9 (35°); 8.1 (40°)	-12.5 ± 1.0	-28.7 ± 3
9-Fluorenone	6.6 (30°); 5.4 (35°); 4.4 (40°)	-7.6 ± 0.3	-15.1 ± 1
Diisobutyl ketone	33.8 (30°); 23.7 (35°); 16.4 (40°)	-13.6 ± 1	-31.6 ± 3
Ethyl pivalate	4.2 (30°); 3.6 (35°); 3.1 (40°)	-5.6 ± 0.3	-9.4 ± 1

[a] ΔS computed from $(\Delta H - \Delta F)/T$, with ΔF in units of atm.$^{-1}$, for 30°.

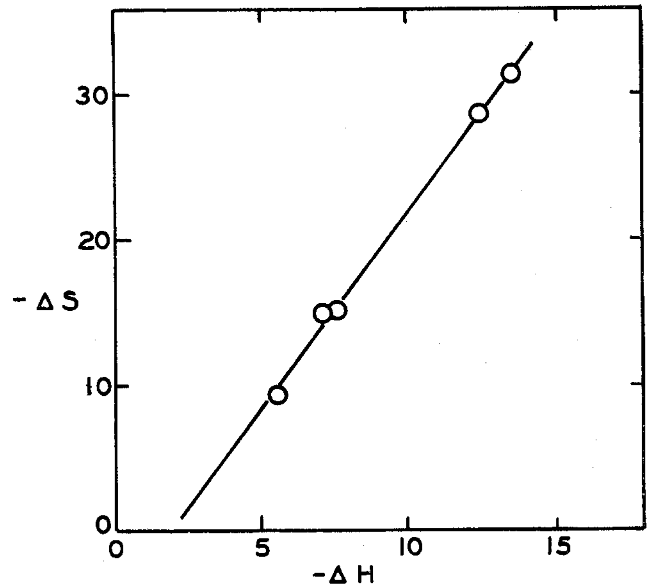

Fig. 1.—Enthalpy–entropy relationship for 1:1 tin(IV) chloride complexes.

the five donors involved in this study. They differ not only in that both nitrogen and oxygen donors are involved, but also in the degree to which adjacent portions of the donor molecule block the donor group. It seems evident that such steric interactions as do exist between donor and acceptor affect the strength of the donor–acceptor bond (and hence affect ΔH and ΔS) without introducing any special orientational requirements on complex formation, which would result in an abnormal enthalpy–entropy relationship. The larger ΔH value for the *p*-methoxybenzonitrile complex as compared with the *p*-chloro is in accord with earlier interpretations of intensity and frequency changes in the nitrile group absorptions.[6]

The results of this investigation, as well as of the previous study, establish the existence in solution of 1:1 addition compounds with tin(IV) chloride. It should be emphasized that the possibility of appreciable dimerization of the 1:1 compounds to form six-coordinate tin complexes is not consistent with the equilibrium constant data. The possibility remains that in benzene solution the solvent occupies a coordination position. This possibility, which is unlikely *a priori*, is apparently ruled out by the fact that the equilibrium constants obtained at 30° for the *p*-chlorobenzonitrile–tin(IV) chloride system in 1,2-dichloroethane are numerically equal to those obtained in benzene at 30°.[3] (The fact that K_{12} bears the same relationship to K_{11} in the two solvents is perhaps more significant than the equality of the corresponding K values.) The evidence, therefore, very strongly indicates a five-coordinate tin species in dilute solutions of tin(IV) chloride with donors.

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Synthesis of Anhydrous Metal Chlorides by Action of Carbon Tetrachloride on the Metal Sulfides

BY ABDO B. BARDAWIL,[1] FRANCIS NASH COLLIER, JR., AND S. YOUNG TYREE, JR.

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The method of Knox and Tyree[2] for the conversion of metal oxides to anhydrous chlorides by action of CCl_4 at 400° in a bomb has been extended to permit replacement of metal oxides by metal sulfides. WS_2, WS_3, MoS_3, and Re_2S_7 give WCl_6, $MoCl_5$, and $ReCl_5$, respectively. The ore, FeS_2, and commercial grades of FeS and MoS_2 give $FeCl_3$ and $MoCl_5$, respectively. Acid-insoluble residues remain after treatment of these lower grades of sulfides.

Experimental

Materials.—Tungstic acid (Matheson Coleman and Bell) was converted to WS_2 or WS_3 by literature methods.[3-5] $Na_2MoO_4 \cdot 2H_2O$ (Merck) and rhenium metal (Department of Chemistry, Univ. of Tennessee) were converted to MoS_3 and Re_2S_7, respectively.[6,7] Iron pyrites, FeS_2 (Staley Consolidated Mine, Staley, N. C.), commercial FeS (Baker and Adamson), and MoS_2 (Climax Molybdenum Co.) were used without purification.

General Procedure.—The appropriate metal sulfide was sealed in a 100 to 130 ml. glass tube along with CCl_4. Eight ml. of

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[1] From work performed in partial fulfillment of requirements for the Ph.D. degree in chemistry at the University of North Carolina, Chapel Hill, N. C.

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