systems containing non-hydrocrabon components.

The pseudo-critical pressures of the hydrocarbon solutions deviate little from the arithmetic means of the values for the components. In the systems involving H_2S or CO_2, however, the deviations are substantial and always negative. The largest values arise when (T_2/T_1) and (P_2/P_1) deviate from unity in opposite directions, *i.e.*, when the molal volumes of the two components differ substantially.

The number of systems studied is not large enough to justify broad conclusions on an empirical basis. It would be desirable to have these quadratic term coefficients for additional systems. Nevertheless, consideration of the various factors affecting intermolecular forces should allow the experienced scientist to estimate values of $(2T_{cm} - T_{c1} - T_{c2})$ and $(2P_{cm} - P_{c1} - P_{c2})$ for systems similar to those listed in Table II with sufficient accuracy for many purposes.

It should be noted that in this study the maximum ratio of critical temperatures of components is 2.4, that of critical pressures is 2.0 and the maximum ratio of critical volumes implied is about 3. We have reason to believe that the behavior of mixed gases may become more complex when the components differ from one another to a greater degree. Thus one should be cautious in extending the present methods outside the range defined above. Nevertheless the present method should yield useful predictions of considerable accuracy for a large variety of solution systems.

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BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE RALPH G. WRIGHT LABORATORY, SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Interaction of Stannic Chloride with Some Organic Bases in Benzene[1,2]

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RECEIVED APRIL 25, 1958

Thermometric titration results confirm the fact that stannic chloride forms AB_2-type addition products with tetrahydrofuran and pyridine in benzene. These results also indicate that with the bases, 1,4-dioxane and morpholine, stannic chloride forms AB-type products in addition to the AB_2-type. Heats of complex formation in dilute benzene solution were measured at 25° and the ΔH^0 values (kcal./mole) for the reactions $A(\text{soln.}) + 2B(\text{soln.}) \rightarrow A_2B(\text{s})$ are: dioxane (-16.9 ± 0.7), morpholine (-47.1 ± 0.9) and pyridine (-39.5 ± 0.8). In the case of tetrahydrofuran, the complex was soluble and the ΔH^0 value obtained was -24.2 ± 0.2. Other thermodynamic quantities were estimated for the pyridine and tetrahydrofuran reactions. Conductance curves for the tetrahydrofuran reaction indicate that ion pairs exist in solution, that the product which precipitates is ionic and that it redissolves in excess base to form a conducting solution.

Introduction

Although proton acid equilibria have been investigated extensively in organic solvents of low dielectric constant, very little work has been done with Lewis acids in these media. Information derived from such studies would bear relevance to the question of acid–base strength, which is important in the investigation of organic reaction mechanisms. This paper presents a study of the interaction of stannic chloride with the bases, 1,4-dioxane, morpholine, tetrahydrofuran and pyridine in the solvent benzene.

Although the reaction products formed in other solvents or in the absence of solvent already have been described in the literature,[3,4] the stoichiometry was investigated in benzene by thermometric titration[5] as well as by the analysis of the products. Enthalpy measurements and equilibrium constants were obtained by a calorimetric procedure.[6] Additional information was obtained from conductance measurements. It was expected that the equilibrium constants might provide a measure of the relative base strengths.

Experimental

Reagents.—Bakers Analyzed Reagent grade stannic chloride was used as received for most experiments, since further purification[7] did not alter the experimental results.

U.S.P. grade thiophene-free benzene (isatin test) was refluxed over phosphorus pentoxide for at least 12 hr. and then distilled from fresh phosphorus pentoxide through a three-foot column packed with Raschig rings. A center cut with $n^{26}\text{D}$ 1.4971 was used. The reported value is $n^{26}\text{D}$ 1.4973.[8] No difference in refraction was observed whether sodium or phosphorus pentoxide was used as drying agent.

Technical grade dioxane was purified by the method of Fieser[9] and distilled from sodium. The center cut was used. It gave $n^{26}\text{D}$ 1.4196 as compared with $n^{25}\text{D}$ 1.4202[10] reported.

Technical grade tetrahydrofuran was dried over phosphorus pentoxide, distilled, then refluxed with lithium aluminum hydride for 12 hr. and finally redistilled from fresh lithium aluminum hydride. The center cut gave $n^{25}\text{D}$ 1.4035. The literature value is $n^{25}\text{D}$ 1.4045.[11]

Pyridine, technical grade, was refluxed over barium oxide for several days and distilled from fresh barium oxide. The center cut gave $n^{25}\text{D}$ 1.5059 as compared with $n^{25}\text{D}$ 1.5067.[12]

U.S.P. grade morpholine was purified by the method of

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(2) This paper represents a part of the work submitted by Mr. Peter R. Segatto to the Graduate School, Rutgers, The State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, November, 1957.

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TABLE I

THERMODYNAMIC DATA AT 25.0 ± 1.0[a]

Reaction	$-\Delta H^0$	K_c	$-\Delta F^0$	$-\Delta S^0$
$SnCl_4$ (soln.) + $2C_4H_8O_2$ (soln.) $\longrightarrow$ $SnCl_4 \cdot 2C_4H_8O_2$(s)	16.9 ± 0.7			
$SnCl_4$ (soln.) + $2C_4H_9ON$ (soln.) $\longrightarrow$ $SnCl_4 \cdot 2C_4H_9ON$(s)	47.1 ± .9			
$SnCl_4$ (soln.) + $2C_5H_5N$ (soln.) $\longrightarrow$ $SnCl_4 \cdot 2C_5H_5N$(s)	39.5 ± .8	10^{10}	14	85
$SnCl_4$ (soln.) + $2C_4H_8O$ (soln.) $\longrightarrow$ $SnCl_4 \cdot 2C_4H_8O$ (soln.)	24.2 ± .2	10^5	7	57

[a] Values of ΔH^0 and ΔF^0 are in kcal. per mole of product for the reactions as written. ΔS^0 is given in entropy units per mole of product. All values apply to the concentration range 3×10^{-3} to 2.2×10^{-2} M initial acid concentration. The mean deviation of at least fourteen determinations is indicated for each ΔH^0.

Friedman, *et al.*,[13] and finally distilled from sodium. The center cut gave n^{25}D 1.4521 as compared with n^{25}D 1.4523[14] reported.

All purifications were performed immediately prior to use and the reagents were protected from moisture by means of drying tubes during refluxing and distillation procedures. They were dispensed in a dry box whose atmosphere was recirculated over large surfaces of phosphorus pentoxide. Dioxane and tetrahydrofuran were tested to ensure the absence of peroxides before use.

Apparatus.—Thermometric titrations were performed in the conventional manner.[5,15] Calorimetric measurements were made in a 250-ml. silvered Dewar flask[16] using a measuring procedure like that of Jordan and Alleman.[17] The calorimeter was calibrated by measuring the heat of neutralization of 0.04833 M hydrochloric acid with 1.000 M sodium hydroxide. The value of ΔH^0 was taken as 13.4 kcal./mole at 25°.[18] Direct current conductance was measured in a flask type cell using a pair of concentric nickel cylinders as electrodes. A micro-microammeter, with 2×10^{-12} ampere current sensitivity, was used in series with the conductance cell and a 300 volt dry battery for current measurement.[2]

Procedure.—Solutions of stannic chloride were prepared in the dry box using a weight pipet[19] and introduced into the apparatus, which was sealed before removal from the dry box. Solutions of base, or pure base, were delivered to the apparatus by means of an automatic constant-delivery-rate buret.[20] Thus the reagents were in contact only with dry glass, except for a very short section of solvent-leached polyethylene tubing used as a connector. Experiments were performed in a room where temperature was maintained at 25.0 ± 1.0°, and all reagents were allowed to reach room temperature before use.

Results

Stoichiometry.—When 0.1 M stannic chloride was titrated with 1 M base in benzene, a fine white crystalline precipitate was obtained in each case. These were slowly soluble in water, producing an acidic solution. They gradually decomposed before melting. The thermometric titration curves (temperature–millimoles of base) changed slope at a molar base to acid ratio of one for dioxane and morpholine, suggesting the composition AB for the product. Similar curves for tetrahydrofuran and pyridine indicate the product AB_2 for those reactions. While these results are in agreement with the literature for tetrahydrofuran and pyridine, the currently suggested composition, AB, for dioxane and morpholine differs from the formula, AB_2, previously reported.[3,4] Analysis of the products obtained in the present study by the method of Sisler, *et al.*,[4] gives AB_2 for all four products, in agreement with the literature. Cobb[21] has shown that a second product, with a base to acid ratio smaller than two, exists for dioxane. When he added equimolar amounts of stannic chloride and dioxane to benzene, the tin was quantitatively recovered in the precipitate. Thus while AB is the more likely composition, A_2B has not been ruled out. Both products are white crystalline solids and the interconversion must be accompanied by an extremely small enthalpy change. This will be considered further under Discussion.

Thermodynamics.—The enthalpy change associated with the formation of each of the products mentioned was determined by the procedure of Dilke and Eley.[6] Several runs in which varying amounts of stannic chloride were mixed with large excesses of base yielded plots of calories *vs.* moles of acid. The slopes of these lines gave ΔH^0. The values obtained are shown in Table I. It should be noted that within the range of acid concentrations used, 3×10^{-3} to 2.2×10^{-2} M, tetrahydrofuran gave no precipitate, while all the other bases did. In contrast, pyridine gives precipitates at acid concentrations as low as 10^{-4} M upon addition of minute quantities of the base. The heats of dilution of the reactants are extremely small compared to the ΔH^0 values.

An estimate of the absolute accuracy of the ΔH^0 values, based upon an analysis of the experimental procedures involved, leads to a maximum determinate relative error of 6%.[2] It will be noted that the precision indicated for each ΔH^0 falls within this limit.

Estimates of K_c were obtained by mixing acid with base in varying mole ratios and measuring the heat evolved.[6] Thus the following equations can be used to calculate K_c for the tetrahydrofuran reaction

$$K = \frac{x}{(a - x)(b - 2x)^2}$$

and

$$K_c = KV^2$$

where

x = moles of product
a = moles of stannic chloride (before reaction)
b = moles of base (before reaction)
V = volume of solution

The quantities a, b and V are carefully measured, while x is determined from the heat measurements and the known value of ΔH^0. Activities are assumed to be equal to the molar concentrations for these dilute solutions, 10^{-3} to 10^{-2} M.

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For the pyridine reaction, K_c is evaluated by means of the equations

$$K = \frac{1}{(a - x)(b - 2x)^2}$$

and

$$K_c = KV^3$$

since the activity of the solid product is taken as unity. No similar calculation can be used for dioxane and morpholine because of the presence of more than one product. Hence, no K_c values were calculated for those reactions.

Since terms in the denominator involve small differences, the relative errors of individual determinations of K_c are large. Therefore a graphical procedure, leading to order-of-magnitude estimates of K_c, was employed. The resultant plots are shown in Figs. 1 and 2, where the solid curves are theoretical graphs for the indicated values of K, and the circles are experimental points. From these estimates of K_c, ΔF^0 and ΔS^0 are computed. These are shown in Table I.

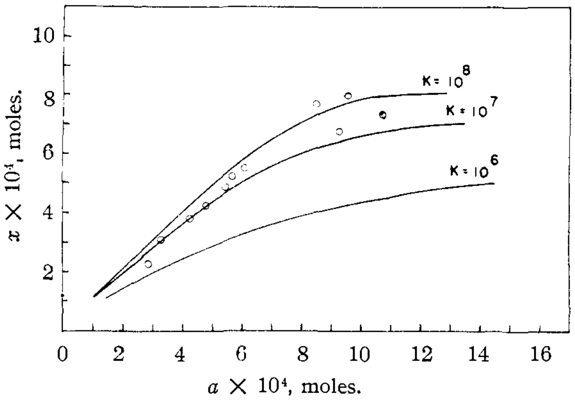

Fig. 1.—Tetrahydrofuran–stannic chloride equilibrium plot.

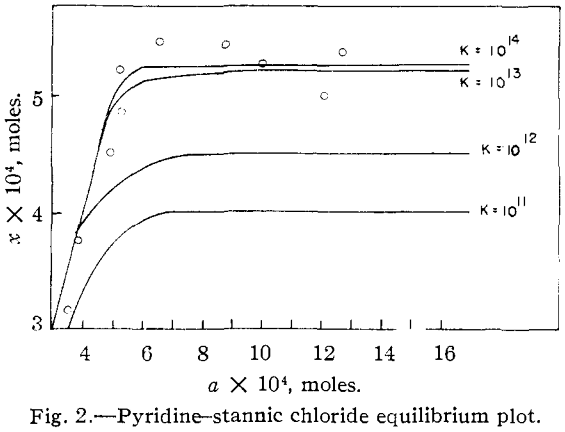

Fig. 2.—Pyridine–stannic chloride equilibrium plot.

Conductance.—Measurements of current were made upon the addition of incremental volumes of tetrahydrofuran solution to stannic chloride in benzene. Initial concentrations of acid ranged between 0.13 and 0.19 *M*. These were titrated with base solutions varying between 0.5 and 0.8 *M*. The conductance cell was maintained in an oil-bath at 25.000 ± 0.005°. Because of the large ΔH^0 for the reaction, readings were taken only after the solution returned to bath temperature as indicated by a thermometer within the cell. The cell constant was 0.03 cm.$^{-1}$, a value obtained by comparison with a cell of known constant. Polarization effects were not expected because of the very small currents involved, but such effects were apparent. Therefore no voltage was applied, and the cell was shorted out, until readings were to be taken. A slower progressive drift in readings than the one caused by polarization was produced by attack of the solution upon the electrodes. It may also have been caused by the entrance of atmospheric moisture, even though precautions were taken to exclude it and no HCl fumes were visible within the conductance cell. Attack on the electrodes was confirmed by the pitting observed after many months of use, and finally by the fact that the electrode supports were cleanly cut by electrolytic attack at the end of about a year of use.

Because the conductance values[2] were not accurate and precisely reproducible, they are not given here. Nevertheless, the values obtained were consistent and significant. When conductance was plotted *vs.* mole ratio of base to acid, all curves showed a smooth rise, reaching a maximum in conductance at a base to acid ratio slightly less than 1.5. The conductance then fell to a minimum at a base to acid ratio somewhat greater than two, and proceeded to rise with almost constant slope. No measurements were made for base to acid ratios greater than five. The maximum was observed to coincide with the onset of precipitation, while the rise in conductance after the minimum was concomitant with dissolution of the precipitate, although the precipitate was not completely dissolved at a base to acid ratio of five. The specific conductance values measured ranged between 0.30 × 10^{-10} and 13.0 × 10^{-10} ohm^{-1} cm.$^{-1}$ while those for the acid and base solutions separately were three orders of magnitude lower.[22]

Discussion

It is clear that the results of thermometric titration agree with the stoichiometry AB_2 reported by other workers[3,4] for the pyridine and tetrahydrofuran complexes of stannic chloride. However, in the cases of dioxane and morpholine, the existence of an AB complex is also suggested by this study. Cobb's[21] work indicates that a second complex does indeed exist, but he fails to prove whether it is AB or A_2B. The latter composition, however, seems unlikely since tin is almost always tetra- or hexa-coördinated, although it has been reported penta-coördinated.[23] On the other hand, no A_2B complexes of this type have been found. Thus stannic chloride could be involved in a bidentate linkage with the two oxygens of dioxane or the oxygen and nitrogen of morpholine. This would require the conversion of dioxane and morpholine from their normal, Sachse-Z-forms at room temper-

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[22] It is interesting to note that if current readings were made before all of the precipitate had settled to a level below that of the electrodes, most of the precipitate would remain suspended in the two-millimeter gap between the electrodes; and it could not be shaken loose. Moreover, the conductance was markedly higher than when the precipitate was allowed to settle. If the voltage were removed and the electrodes short circuited, however, the precipitate would immediately settle, with an attendant drop in conductance.

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ature[24] to their U-forms. Yet this conversion has been assumed in explaining the "bidentate" linkage in the nitrogen tetroxide–dioxanate complex of the AB type.[25] It is interesting to note that triphenylmethyl bromide forms a one-to-one crystalline addition compound with stannic bromide.[26]

A close examination of the thermometric titration curves for dioxane reveals that the slope is perceptibly, but not measurably, different from zero after the change at the molar base to acid ratio of one; and that it fails to become zero at a ratio of two. The same is true for morpholine, but the slope is slightly greater. It must be emphasized that these are not heats of dilution, which are much smaller. Rather, these slopes must be associated with the slow, heterogeneous conversion of the AB complexes to the AB_2 type. The heats of conversion are extremely small—less than 10% of the ΔH^0 values—but that for morpholine is larger than the one for dioxane. This is to be expected, because if both oxygens were bonded to tin in the AB complex, the formation of AB_2 would require the breaking of one oxygen–tin bond with the formation of another oxygen–tin bond, and the energy change involved should be close to zero. On the other hand, the conversion of AB to AB_2, for morpholine, involves the rupture of an oxygen–tin bond with the formation of a nitrogen–tin bond, resulting in the evolution of energy, because nitrogen is a better electron donor than oxygen. A comparison of the ΔH^0 value given here for dioxane, Table I, with that of Zenchelsky, *et al.*,[5] obtained for nearly equimolar mixtures of stannic chloride and dioxane in benzene, shows that the heat of conversion is no greater than two hundred calories per mole of product. This is less than the experimental error of the ΔH^0 values.

The conductance studies of the stannic chloride–tetrahydrofuran system show that the soluble complex does consist of ion pairs, as would be expected.[26,27] They further show that the precipitate is ionic and that it dissolves in the presence of excess base to form ion pairs in solution. Since no marked change in slope of the conductance curve is observed after dissolution of the precipitate begins, and up to a base to acid ratio of five, it would appear that only one new species is formed. The species in solution before precipitation is evidently $(C_4H_8O)_2SnCl_3^+$, Cl^- while that after dissolution begins may be $(C_4H_2O)_3SnCl_3^+$, Cl^-.[28]

The ΔF^0 values calculated for the pyridine and tetrahydrofuran complexes (Table I) are in the order expected. Nitrogen is the stronger electron donor; and, moreover, the pyridine reaction involves the additional step of crystallization. However, a direct comparison of the strengths of the two bases is impossible. To do so would require knowing the concentration of undissociated complex in equilibrium with reactants and precipitate. Yet this method will permit a comparison of base strengths when the reactions involved are homogeneous. The observed entropy changes are large but not unreasonable for a case where one molecule is formed from three.

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[28] The first ion pair is analogous to that postulated by Van Dyke for $(CH_3OH)_2AlBr_3$; see R. E. Van Dyke, THIS JOURNAL, **73**, 398 (1951).

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY AND DUQUESNE UNIVERSITY]

Ion-exchange and Solvent-extraction Studies on Co(II) and Zn(II) Complexes of Some Organic Acids[1]

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The stability of the Co(II) and Zn(II) complexes of bioxalate, oxalate, citrate and glycolate have been determined by the use of Co-60 and Zn-65 in conjunction with the methods of ion exchange and solvent extraction. It is demonstrated that both the stability of the glycolate complexes and the ion-exchange distribution coefficients of the tracer metals decrease with increase in ionic strength. An important assumption in the use of ion-exchange method for complex study is that the uptake of the complex itself by the cation exchanger is nil or very small relative to the uncomplexed cation. This is demonstrated directly for Mg(II) complex of oxalate by means of oxalate labeled with C-14. In ion-exchange experiments the uptake of Co(II) and Zn(II) in the presence of imidazole is higher than in the absence of imidazole, while in corresponding solvent-extraction experiments, the opposite is true. These results indicate that the +2 imidazole complexes themselves are taken up by the cation exchanger and show that the ion-exchange and solvent-extraction experiments complement each other in the study of metal complexes.

Introduction

Recently Li, *et al.*,[2] obtained the formation constants of uranyl complexes of glycolic and oxalic acids, using the methods of ion exchange and solvent extraction. They showed that even in 1 and 2 *M* $HClO_4$, uranyl complex with $H_2C_2O_4$ does not

[1] Work done in part at Argonne National Laboratory under the auspices of the U. S. Atomic Energy Commission. The work of N. C. Li and R. Pfleger was supported in part by the U. S. Atomic Energy Commission through Contract No. AT(30-1-)-1922 with Duquesne University.

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