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LEWIS ACID-BASE TITRATIONS EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

PART III. PREPARATION, ISOLATION AND CHARACTERIZATION OF SOME ADDUCTS PREDICTED FROM TITRATION CURVES

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During an investigation of the use of megacycle-frequency oscillators to follow Lewis acid-base titration reactions[1,2], it was noted that precipitates frequently formed during the course of the titration, especially when aluminum chloride was used as the Lewis acid. While the adducts involving stannic chloride as the Lewis acid were usually soluble at the concentrations and in the solvents used, insoluble products could be obtained by changing the solvent, increasing the concentrations of the reactants, or a combination of the two.

The isolation in pure form of several of these reaction products was then attempted; one reason was the desire to verify the composition of adducts indicated by the characteristic shapes of the megacycle-frequency titration curves. Isolation of several of the adducts of interest has been reported in the literature, but characterizing data such as elemental composition and melting point are lacking for most of these.

Consequently, a number of adducts involving aluminum chloride and stannic chloride, and various nitrogen and oxygen bases were prepared, generally by mixing solutions containing the probably stoichiometric amounts of acid and base dissolved in acetonitrile, benzene or *n*-heptane.

DISCUSSION AND CONCLUSIONS

Thirteen stannic chloride–oxygen base adducts were prepared and analyzed for tin

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TABLE I

NATURE AND COMPOSITION OF SOLID STANNIC CHLORIDE–OXYGEN BASE ADDUCTS

Base used	Character of precipitate	M.P.[b] (°)	Analysis[c]		Cl : Sn ratio	Possible product (%)[d]	purity (%)[e]
			Cl(%)	Sn(%)			
Diethyl ether							
$SnCl_4 \cdot 2Et_2O$[a]	White powder	78–80	34.3	28.1	4.08	99	97
			34.7	29.0	4		
n-Dibutyl ether							
$SnCl_4 \cdot 2Bu_2O$[a]	White needles	37–39	24.2	21.1	3.84	89	92
			27.1	22.8	4		
Tetrahydrofuran							
$SnCl_4 \cdot 2THF$[a]	White powder	S : 165–175	35.0	29.1	4.01	100	99
			35.0	29.3	4		
p-Dioxane							
$SnCl_4 \cdot D$*	White powder	S : 175–195	38.0	31.3	3.85	94*	92
$SnCl_4 \cdot 2D$			40.6	33.9	4		
			32.3	27.1	4		
Methyl alcohol	Pasty white solid	98–103	42.8	36.4	3.96	98*	100
	White crystals[f]	175–200	36.8	40.1	3.07	100**	97
$SnCl_4 \cdot 2MeOH$*			43.7	36.6	4		
$SnCl_3 \cdot OMe \cdot MeOH$**			36.9	41.2	3		
Ethyl alcohol	Pasty white solid	53–56	38.0	33.1	3.85	95*	98
	White needles[g]	191–193	33.8	37.5	3.02	101**	100
$SnCl_4 \cdot 2EtOH$*			40.2	33.1	4		
$SnCl_3 \cdot OEt \cdot EtOH$**			33.8	37.5	3		
n-Propyl alcohol	White crystals	95–98	36.9	30.9	4.00	99*	99
	White crystals[f]	182–184	30.9	34.0	3.05	100**	99
$SnCl_4 \cdot 2PrOH$*			37.3	31.2	4		
$SnCl_3 \cdot OPr \cdot PrOH$**			30.9	34.5	3		
iso-Propyl alcohol	White powder[f]	103–106	37.1	31.5	3.95	100*	101
	White needles[f]	104–106	36.8	30.8	4.00	99*	99
$SnCl_4 \cdot 2PrOH$*			37.3	31.2	4		
$SnCl_3 \cdot OPr \cdot PrOH$			30.9	34.5	3		
n-Butyl alcohol	White needles	?	33.8	29.0	3.91	97*	100
$SnCl_4 \cdot 2BuOH$*			34.7	29.0	4		
$SnCl_3 \cdot OBu \cdot BuOH$			28.6	31.9	3		
$SnCl_3 \cdot OBu$			35.7	39.8	3		
tert.-Butyl alcohol	White powder	70[f]	33.5	37.2	3.01	94*	93
$SnCl_4 \cdot 2BuOH$			34.7	29.0	4		
$SnCl_3 \cdot OBu \cdot BuOH$			28.6	31.9	3		
$SnCl_3 \cdot OBu$*			35.7	39.8	3		

Water	White crystals[b]	56–58	40.9	34.9	3.93	101*	103
SnCl₄·6H₂O			38.5	32.2	4	96**	98
SnCl₄·5H₂O			40.5	33.9	4		
SnCl₄·4H₂O**			42.6	35.7	4		
Acetone	White powder	94–96	37.0	31.3	3.93	98	99
SnCl₄·2A			37.7	31.5	4		
Cyclohexanone	Tan granular solid	74–76	39.4	24.6	3.98	95	95
SnCl₄·2CH			31.0	26.0	4		

a Possible compositions of solid, which precipitated from heptane solution, are given in every case.
b Sublimation temperature designated by a prefix "S".
c Each percentage is the average of duplicate determinations; the average deviation was frequently less than 0.1%.
d Based on the ratio of chloride in the product formed to the chloride in a possible species indicated by * or ** when more than one possible species is given.
e Based on the ratio of tin in the product formed to the tin in a possible species indicated by * or ** when more than one possible species is given.
f Product initially prepared was then recrystallized from heptane.
g Product initially prepared was then recrystallized from benzene.
h Prepared by bubbling moist air through a benzene solution of stannic chloride.
i Decomposed, i.e., turned brown; did not melt even at higher temperatures.

and chloride ion; melting or sublimation points were determined for ten of them. Table I summarizes the data obtained and includes calculated percentages of tin and chlorine corresponding to possible formulas for the adducts, the Cl : Sn ratio found, and purities calculated on the basis of the ratios of Sn and Cl in the product obtained to the Sn and Cl in a possible product.

Stannic chloride–ether adducts

Molecular addition compounds involving stannic chloride and oxygen bases were reported in the literature as early as 1841, when a $SnCl_4$–Et_2O adduct was reported but not characterized[3]. Much later, stable addition compounds of stannic chloride and various esters, as well as diethyl ether, were reported[4]. More recently, SISLER and coworkers[5–9] have systematically studied the molecular addition compounds of the Group IV tetrahalides with ethers. Addition compounds of stannic chloride reported are a AB_2 adduct with diphenyl ether[8], AB and AB_2 adducts with methyl m-cresyl ether[9] and AB_2 adducts with both tetrahydrofuran (THF) and tetrahydropyran[6]. Melting points were given for several of these compounds.

Adducts of stannic chloride with diethyl ether, n-dibutyl ether, and THF prepared in the present study were all AB_2 adducts based on the Sn and Cl content. While the megacycle-frequency response curve for the addition of THF to $SnCl_4$ in benzene[2] had a maximum at the 1 : 1 molar ratio, it was not possible to isolate a solid AB species. Even when mixtures containing a considerable molar excess of $SnCl_4$ over THF were used, the adduct formed was always the AB_2 product. This, of course, does not mean that the AB adduct does not exist in solution, but merely indicates the greater stability and/or lower solubility of the AB_2 adduct over the AB adduct.

The only adduct of stannic chloride and p-dioxane that could be isolated was the AB compound. Attempts to isolate the AB_2 and A_2B adducts were unsuccessful. These results are in agreement with the megacycle-frequency response curve for the addition of pure p-dioxane to stannic chloride in benzene; a definite break in the curve occurs only at the 1 : 1 molar ratio[2]. ZENCHELSKY et al.[10] also reported 1 : 1 stoichiometry for thermometric titration involving stannic chloride and p-dioxane. Formation only of a AB species is in conformity with the behavior of p-dioxane as a diacid Lewis base. The resulting $SnCl_4$–dioxane compound then has hexacoordinate tin with the dioxane most likely serving as a bridging ligand between two tin atoms, which would result in a linear polymeric molecule (*cf.* ref.[2]).

The melting points obtained for the $SnCl_4$–Et_2O and $SnCl_4$–THF adducts agree well with those reported in the literature; the $SnCl_4$–n-Bu_2O adduct is a new compound. Analytical and melting point data have not been previously reported for the $SnCl_4$–p-dioxane adduct.

Stannic chloride–alcohol adducts

An adduct reported in 1884[11] involving stannic chloride and ethyl alcohol was assigned the formula $SnCl_3(OEt)(EtOH)$. The simple dialcoholate was subsequently prepared[12]. More recent investigation[13] indicates that $SnCl_3(OR)ROH$, $SnCl_4$·$2ROH$, or a mixture of the two is generally obtained. The latter, when heated, gave a sublimate of the simple dialcoholate. When pure $SnCl_3(OMe)MeOH$ was heated under reduced pressure, the volatile $SnCl_4$ · $2MeOH$ was obtained, probably by a disproportionation,

$$2SnCl_3(OMe)MeOH \rightarrow SnCl_4(MeOH)_2 + SnCl_2(OMe)_2 \qquad (1)$$
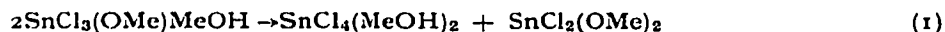
$SnCl_3(OEt)EtOH$ was shown to be dimeric in boiling benzene, with tin exhibiting the coordination number of six as in the monomeric tetrachloride dialcoholates. The initial products for tert.-butyl and tert.-amyl alcohols were again mixtures, but under pressure monoalcoholates sublimed; the latter likely formed in preference to the characteristic dialcoholates because of the steric effect of the tertiary alkyl group in preventing the approach of the second alcohol molecule.

The composition of the adducts formed by stannic chloride with methyl, ethyl, n-propyl and n-butyl alcohols in the present study seem to be temperature-dependent and are generally in good agreement with those reported by BRADLEY, CALDWELL AND WARDLAW[13]. Initial precipitates obtained at room temperature were the simple AB_2 adduct, i.e., $SnCl_4 \cdot 2ROH$. Upon recrystallization from boiling solvent, these products change to $SnCl_3(OR)ROH$ through the elimination of a molecule of hydrogen chloride. The n-butyl alcohol adduct seemed to decompose when recrystallization was attempted; a product was not obtained.

The simple iso-propyl alcohol adduct, $SnCl_4 \cdot 2C_3H_7OH$, apparently underwent no change upon recrystallization. In the case of tert.-butyl alcohol, the adduct initially formed analyzed for $SnCl_3 \cdot OC_4H_9$ and did not change upon recrystallization.

It seems clear that alcohols tend to form the simple dialcoholate with stannic chloride. This was predicted by the characteristic curve maxima at 2 : 1 molar ratio ($ROH : SnCl_4$) in the megacycle-frequency response curves for the addition of alcohols to stannic chloride in benzene (cf. ref.[2]).

Whether or not a molecule of hydrogen chloride can be eliminated from the dialcoholate seems to depend on the nature of the alcohol involved and the temperature. In the case of tert.-butyl alcohol, the failure to form the AB_2 adduct is likely due to the influence of steric factors, which prevent the approach of more than the one alcohol molecule to the stannic chloride molecule.

DEVLIN AND PEPPER[14] report a AB_3 adduct of stannic chloride and ethyl alcohol, but this conclusion does not seem justified. The formula was based solely on a chlorine analysis of the adduct. Although the 35.5% Cl found is very close to the 35.7% calculated for the AB_3 adduct, it is not too far from that calculated for $SnCl_3(OC_2H_5)$-C_2H_5OH (33.6%). Since a tin determination was not made on the product, a Cl : Sn ratio of 4 : 1 was not substantiated. The melting point reported by DEVLIN AND PEPPER for their product is the same as that obtained for the $SnCl_3(OC_2H_5)C_2H_5OH$ compound in the present study. It, therefore, seems quite possible that DEVLIN AND PEPPER were working with the latter compound instead of $SnCl_4 \cdot 3C_2H_5OH$.

Other stannic chloride adducts

The adduct formed between stannic chloride and water appears to be $SnCl_4 \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$ or a mixture of the two, based on both analysis and melting point. Acetone and cyclohexanone clearly form AB_2 adducts with stannic chloride.

Aluminum chloride adducts

Anhydrous aluminum chloride readily combines with ammonia. While the mono- and triammines are the most stable[15], other adducts have been reported[16]. Although ELEY[17] states that evidence indicates that only the 1 : 1 adducts of aluminum

chloride with nitrogen bases, other than ammonia, have been isolated, VAN DYKE and co-workers[18,19] report conductance measurements and vapor pressure studies, which indicate the formation of AB_2 adducts with trimethylamine, pyridine and benzonitrile in nitrobenzene and benzonitrile. However, the solid adducts were not actually isolated and analyzed.

Table II summarizes the analyses of the three aluminum chloride–nitrogen base adducts prepared in the present study, the Cl : Al ratios found along with the Cl : Al ratios for possible formulas, and the calculated purity based on the ratios of Al and Cl in the product obtained to those in a possible product.

Acetonitrile forms a AB_2 adduct with aluminum chloride. It was impossible, by the technique used, to isolate a 1 : 1 adduct. The unexpected AB_3 adduct seems to have formed in the reaction of piperidine with aluminum chloride. These two adducts support the view that aluminum chloride can form adducts with nitrogen bases in other than a 1 : 1 ratio.

The reaction of aluminum chloride with pyridine gives an interesting product; it is clear that two chlorine atoms have been removed from the aluminum chloride molecule as the 1 : 1 pyridine–aluminum chloride adduct has formed, since the Cl : Al ratio in the adduct is 1 : 1. The AB_2 aluminum chloride–pyridine adduct could not be prepared by the technique used, although the megacycle-frequency response curve for the addition of pyridine to a solution of aluminum chloride in acetonitrile[1] indicates the formation of both the AB and AB_2 adducts.

TABLE II

NATURE AND COMPOSITION OF SOLID ALUMINUM CHLORIDE–NITROGEN BASE ADDUCTS

Base used	Analysis		Cl : Al ratio	Possible product purity	
	Cl(%)	Al(%)		(%) [c]	(%) [a]
Acetonitrile	47.6	12.7	2.85	96*	101
$AlCl_3 \cdot \overline{AC}$[a]	61.0	15.5	3		
$AlCl_3 \cdot 2\overline{AC}$*	49.4	12.5	3		
Piperidine	25.8	6.4	3.06	94*	92
$AlCl_3 \cdot pip$	48.6	12.4	3		
$AlCl_3 \cdot 2pip$	35.1	8.9	3		
$AlCl_3 \cdot 3pip$*	27.4	7.0	3		
Pyridine	25.1	20.1	0.96	99	105
$AlCl \cdot py$	25.2	19.2			

[a] Possible compositions of solid, which precipitated from heptane solution, are given in every case.
[b] Based on the ratio of chloride in the product formed to the chloride in a possible species indicated by * when more than one possible species is given.
[c] Based on the ratio of aluminum in the product formed to the aluminum in a possible species indicated by * when more than one possible species is given.

EXPERIMENTAL

Chemicals

n-Heptane (Eastman Kodak yellow label) was purified as follows[20]. 1 l was vigorously stirred with 200 ml of concentrated sulfuric acid for at least 4 h, washed twice

with water, dried over anhydrous calcium sulfate, and distilled through an 18-inch Fenske column; the absence of unsaturated contaminants was verified by the ultra-violet spectra. Other chemicals used were identical to those used in the titration studies[1,2].

Preparation of adducts

Ten to 20 mmoles of pure oxygen base was added to 10–20 mmoles of stannic chloride in 20 ml of *n*-heptane or benzene contained in a 50-ml glass-stoppered flask; in every case the solid adduct obtained was independent of the proportions used. Immediate precipitation occurred except with stannic chloride and *n*-dibutyl ether; the latter mixture required cooling with Dry Ice–acetone for precipitation to occur. Precipitates were filtered, washed with pure solvent, and air-dried before being transferred to weighing bottles. All operations except Dry-Ice cooling were carried out in a dry box. During the cooling operation the reaction mixture was kept in a glass-stoppered conical flask, and then immediately returned to the dry box for filtration and further processing.

Use of a special sintered glass filtering crucible (Fig. 1) permitted preparation, washing, drying and weighing of the aluminum chloride–nitrogen base adducts
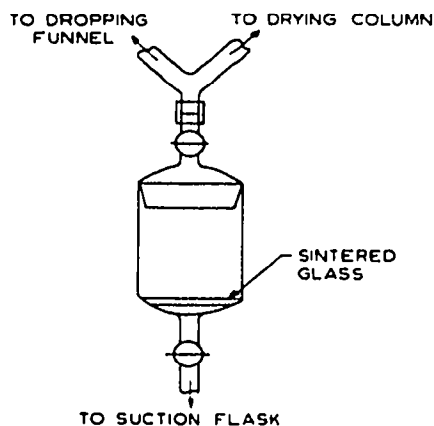

Fig. 1. Sintered glass filtering crucible used in the preparation of aluminum chloride–nitrogen base adducts.

without contact with the atmosphere. Twenty to 30 ml of approximately 0.4 *M* aluminum chloride in acetonitrile was delivered from an automatic buret to a 125-ml separatory funnel; a two or three molar excess of 0.1 *M* base in acetonitrile was immediately added. After brief shaking, the funnel was connected to the previously weighed filtering crucible; the precipitate was filtered by suction, washed with anhydrous solvent from the dropping funnel, and dried by drawing dry air through the apparatus for 10–15 min (a 4-ft. length of 18-mm glass tubing filled with anhydrous calcium sulfate served as the drying column). After closing of the stopcocks, the filtering crucible was detached and reweighed to determine the weight of the adduct.

The adduct from aluminum chloride and acetonitrile was formed by pumping off excess solvent from a 25-ml portion of 0.175 *M* aluminum chloride in acetonitrile, using a side-arm tube attached to a vacuum pump. A glass-like solid remained as the container approached constant weight.

Analysis of the adducts

Samples of the stannic chloride–oxygen base adducts were weighed out from weighing bottles, which were tightly stoppered and stored in a desiccator. Tin was determined gravimetrically, following hydrolysis to the hydrous oxide in boiling aqueous 2% ammonium nitrate solution; the precipitate was filtered through Whatman No. 41H paper, washed free of chloride with 2% ammonium nitrate solution, ignited, and weighed as SnO_2. Chloride was determined in the filtrate by potentiometric titration with 0.1 M silver nitrate.

In the case of the aluminum chloride–nitrogen base adducts, the crucible containing the weighed product was placed in a 250-ml beaker containing water. After soaking for several minutes, the crucible was removed with thorough rinsing with distilled water to remove all of the product. A slight excess of dilute ammonia and filter pulp were added; the solution was boiled for 1 min to coagulate the hydrous alumina precipitate, which was filtered through Whatman No. 41H paper, washed with hot 2% ammonium nitrate solution until washings were chloride-free, ignited, and weighed as Al_2O_3. The accuracy of this method for the determination of aluminum was verified by a control determination on reagent grade aluminum chloride hydrate. One ml of 6 M nitric acid was added to the filtrate from the aluminum filtration and the chloride titrated potentiometrically with 0.1 M silver nitrate.

Melting points of the adducts were taken by the conventional capillary technique. A Thiele tube, containing dibutyl phthalate and heated with a microburner, served as the bath. The 250° thermometer used was calibrated against one certified by the National Bureau of Standards. Because of the extreme reactivity of the aluminum chloride adducts with atmospheric moisture, their melting points could not be determined by the technique employed.

SUMMARY

Adducts of stannic chloride with thirteen oxygen bases, isolated as solids from benzene or heptane solution, were characterized by analysis and melting point behavior; several of these are new compounds. Diethyl ether, *n*-dibutyl ether and tetrahydrofuran form AB_2 adducts; *p*-dioxane, in conformity with its being a diacid base, forms only a 1 : 1 species. Methyl, ethyl, *n*-propyl and *n*-butyl alcohols form simple AB_2 adducts at room temperature which on recrystallization from boiling solvent give $SnCl_3(OR)ROH$; iso-propyl alcohol gives only the AB_2 adduct; *tert.*-butyl alcohol only forms $SnCl_3 \cdot OC_4H_9$ (steric hindrance probably prevents formation of the AB_2 adduct). Water gives a AB_4 or AB_5 adduct.

Adducts of aluminum chloride with three nitrogen bases were similarly prepared from acetonitrile solution. Pyridine forms a 1 : 1 species. Acetonitrile itself forms a AB_2 species. Piperidine forms a AB_3 species. The latter two adducts support the view that $AlCl_3$ can form other than 1 : 1 adducts with nitrogen bases.

RÉSUMÉ

Les auteurs ont effectué la préparation, la séparation et la caractérisation des produits d'addition du chlorure stannique, obtenus avec 13 bases oxygénées. Plusieurs d'entre eux sont des composés nouveaux. De même, les produits d'addition du chlorure d'aluminium avec 3 bases azotées ont été préparés.

ZUSAMMENFASSUNG

Beschreibung der Herstellung, Trennung und Eigenschaften der Additionsprodukte von Zinntetrachlorid mit Sauerstoffbasen sowie von Aluminiumchlorid mit Stickstoffbasen.

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