

LEWIS ACIDITY OF ORGANOGERMANIUM CHLORIDES

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Summary

The reactions of some organogermanium chlorides with Lewis bases have been studied calorimetrically in benzene solution. Ph_3GeCl shows no Lewis acidity. Me_2GeCl_2 forms a 1/2 adduct with NBU_3 , 1/1 adducts with pyridine or 4-methylpyridine and does not react with 2,2'-bipyridine, PBU_3 or O-donors. PhGeCl_3 forms 1/2 adducts with pyridine, 4-methylpyridine or 2-methylpyridine, 1/1 adducts with 2,2'-bipyridine, PBU_3 or pyridine *N*-oxide. While the enthalpies of formation of the adducts are often slightly larger than those of corresponding tin compounds, adducts of the germanium compounds are much less stable, showing that the germanium atom is readily sterically overcrowded.

Introduction

It has long been known that tetrahedral compounds of the group IV elements, silicon, germanium, tin and lead, may react with Lewis bases to give addition compounds or complex ions in which the coordination number of the central atom is increased to five, six or, in a few cases, even further.

The Lewis acidity of germanium compounds has been much less extensively studied than that of silicon or tin compounds. A 1/1 adduct of germanium tetrachloride with trimethylamine has been isolated, infrared studies made [1] and its crystal structure determined: the germanium atom is 5-coordinate and the N atom occupies an axial site in the $\text{GeCl}_4 \cdot \text{NMe}_3$ molecule [2]. The 1/1 adduct of GeCl_4 with pyrrolidine is also probably 5-coordinate [3].

With pyridine GeCl_4 forms a 2/1 adduct, GeCl_4py_2 , shown by X-ray analysis to have a 6-coordinate, *trans*-octahedral structure [4]. Similar adducts are known with isoquinoline [5], piperazine and acridine [3]; adducts of GeF_4 and GeBr_4 with two molecules of pyridine or isoquinoline have also been obtained

[5], as have those of GeF_4 with dimethylsulphoxide or dimethylformamide [6]. An incomplete X-ray analysis of the adduct of GeF_4 with 2,2'-bipyridine shows the GeF_4bipy molecule to have a distorted *cis*-octahedral structure [7] and GeCl_4bipy and GeBr_4bipy have been shown to be non-electrolytes in nitrobenzene [8]. A 1/2 adduct of GeCl_4 with 1,10-phenanthroline is also known, but the base is probably not chelate [3]. Infrared studies have been made of a phosphine adduct $\text{GeCl}_4(\text{PMe}_3)_2$ [1,9].

The 1/2 adducts GeX_4B_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{B} = \text{pyridine}$ or isoquinoline) are sparingly soluble in organic solvents and heats of formation of the crystalline compounds have been determined calorimetrically by precipitation from hexane or nitrobenzene [5], but without knowledge of the energies of crystallisation these data are of limited value in assessing the strengths of GeX_4 as Lewis acids.

We have previously reported thermodynamic data, obtained by calorimetric titration in benzene or acetonitrile solution, for the addition of a wide variety of bases to organotin chlorides [10,11,12] and organosilicon chlorides [13]. There do not appear to have been any previous studies of organogermanium compounds as Lewis acids, except an observation that Ph_2GeCl_2 does not react with 2,2'-bipyridine [8]. We now report thermodynamic data for the reactions of a small number of bases with Me_2GeCl_2 , PhGeCl_3 and GeCl_4 in benzene solution.

Experimental

Organogermanium compounds and GeCl_4 were obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, California and purified by distillation before use; purity was checked by C, H and Cl analyses. Several germanium compounds were examined but, apparently because of scrambling on distillation, we had difficulty in obtaining highly pure samples from the rather small quantities available and only Me_2GeCl_2 , PhGeCl_3 , Ph_3GeCl and GeCl_4 could be obtained in sufficiently pure form for calorimetric work.

Bases were obtained from various sources and purified by distillation or crystallisation as appropriate; liquid bases were dried and stored over anhydrous potassium carbonate. Benzene for use as solvent was purified by freezing, followed by distillation and dried and stored over calcium hydride.

Calorimetric titrations were carried out on a LKB 8700 calorimeter at 30°C using the previously described technique [14]. Briefly, a benzene solution of base was titrated incrementally into 100 ml of a benzene solution of the germanium compound and the heat change recorded after each addition of titrant. All solutions were handled throughout in an atmosphere of dry nitrogen. Control titrations were carried out to determine the heat of dilution of the titrant. Enthalpies of reaction were calculated from the extrapolated, integrated heats of reactions after correction and equilibrium constants, K , calculated at each point in the titration; the enthalpy was then refined iteratively to give constant values of K . Values of ΔH^0 in the tables are the average of at least three determinations over the indicated range of concentrations of the germanium compound; uncertainties in ΔH^0 are mean deviations. Values of K are the average of at least three determinations and uncertainties are the sum of the mean deviation and the average standard deviation in individual titrations.

Results and discussion

Preliminary experiments gave no evidence of reaction of Ph_3GeCl with bases, but germanium compounds containing more than one chlorine atom reacted with evolution of heat. A crystalline adduct isolated from solutions of Me_2GeCl_2 and tributylamine was shown by analysis to be $\text{Me}_2\text{GeCl}_2\text{NBU}_3$. (Found: C, 57.3; H, 11.1; N, 5.5. $\text{C}_{14}\text{H}_{33}\text{Cl}_2\text{GeN}$ calcd.: C, 57.4, H, 11.1, N, 5.2%.) Several other adducts were isolated but only in less pure form; as has been previously reported [7] we found the organogermanium chlorides to be much more sensitive to traces of moisture than the corresponding tin compounds.

The calorimetric titrations show that in benzene solution Me_2GeCl_2 forms 1/1 adducts of very low stability with pyridine or 4-methylpyridine; thermodynamic data are given in Table 1. The bases, 2,2'-bipyridine, dioxan, dimethylsulphoxide and tributylphosphine gave no evidence of reaction.

Comparison with Me_2SnCl_2 [10] shows that Me_2GeCl_2 is a much weaker Lewis acid: thus, Me_2SnCl_2 reacts with pyridine giving first $\text{Me}_2\text{SnCl}_2\text{py}$, with $K_1 = 17 \text{ l mol}^{-1}$, $\Delta H_1^0 = -45 \text{ kJ mol}^{-1}$, then $\text{Me}_2\text{SnCl}_2\text{py}_2$, with $K_2 = 13$, $\Delta H_2^0 = -28$. The rather larger enthalpy of formation of $\text{Me}_2\text{GeCl}_2\text{py}$ compared to $\text{Me}_2\text{SnCl}_2\text{py}$ presumably arises from the smaller size of the germanium atom, but the lower stability of the germanium compound and the restriction of the coordination number to five show that the germanium atom is readily overcrowded. This is further supported by the failure of Me_2GeCl_2 to react with 2,2'-bipyridine, though the tin compound forms a moderately stable 1/1 adduct, with $K = 123$ and $\Delta H^0 = -65$. The tin compound also forms both 1/1 and 1/2 adducts with pyridine *N*-oxide [15] and a 1/1 adduct with PBU_3 . The only base with which Me_2GeCl_2 formed a 1/2 adduct is tributylamine (data in Table 2) and in this case the corresponding tin compound undergoes disproportionation in the presence of the base.

As in the series of organotin compounds reactivity increases as the number of chlorine atoms increases and PhGeCl_3 gives 1/1 adducts with 2,2'-bipyridine and PBU_3 (Table 1). These adducts are again of much lower stability than the corresponding tin compounds, for which $K > 10^5$, though there is little difference between the enthalpies of formation, again showing that the low stability of the PhGeCl_3 adducts is steric in origin. The lower reactivity of the germa-

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF LEWIS BASES WITH ORGANO-GERMANIUM CHLORIDES IN BENZENE SOLUTION AT 30°C. Conc. of Ge compounds in mmol l^{-1} , K in l mol^{-1} , ΔH^0 , ΔG^0 in kJ mol^{-1} , ΔS^0 in $\text{J K}^{-1} \text{mol}^{-1}$

Ge compound	Base	[Ge]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
Me_2GeCl_2	py	4.9–10.5	2.2 ± 0.3	52.8 ± 3.5	1.9 ± 0.4	168 ± 13
Me_2GeCl_2	4-mepy	0.7–2.2	6.3 ± 1.0	69.6 ± 3.4	4.6 ± 0.4	214 ± 13
PhGeCl_3	bipy	0.7–1.0	16.4 ± 0.9	123.2 ± 2.7	7.0 ± 0.2	383 ± 9
PhGeCl_3	PBU_3	1.3–1.8	59.9 ± 3.3	108.4 ± 0.9	10.3 ± 0.2	324 ± 4
PhGeCl_3	py-NO	0.5–0.7	116 ± 4	88.2 ± 3.3	12.0 ± 0.2	252 ± 12

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1/2 ADDUCTS OF ORGANOGERMANIUM CHLORIDES WITH LEWIS BASES IN BENZENE SOLUTION AT 30°C. Conc. of Ge compound in mol l⁻¹, *K* in l² mol⁻², ΔH^0 , ΔG^0 in kJ mol⁻¹, ΔS^0 in J K⁻¹ mol⁻¹.

Ge compound	Base	[Ge]	<i>K</i>	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
Me ₂ GeCl ₂	NBu ₃	0.9–1.1	∞	135.5 ± 0.7		
PhGeCl ₃	py	1.0–2.4	3 × 10 ⁴	177.9 ± 1.9	26.1 ± 0.4	501 ± 8
PhGeCl ₃	4-mepy	0.9–1.7	3 × 10 ⁵	176.9 ± 17.5	31.7 ± 0.3	479 ± 59
PhGeCl ₃	2-mepy	1.1–1.3	1 × 10 ⁵	171.8 ± 6.1	29.3 ± 0.2	470 ± 21
GeCl ₄	PBu ₃	1.0–1.7	∞ ^a	87.9 ± 2.8		
			4380 ± 390 ^b	108.1 ± 2.0	21.1 ± 0.2	287 ± 7

^a For addition of first PBu₃. ^b For addition of second PBu₃.

niun compound is also shown with pyridine *N*-oxide which gives only a moderately stable 1/1 adduct, whereas PhSnCl₃ gives a 1/2 adduct of much higher stability [15].

Both PhGeCl₃ and PhSnCl₃ give 1/2 adducts with pyridine or 4-methylpyridine. Data for the formation of the germanium compounds are given in Table 2, which also includes data for the formation of 1/1 and 1/2 adducts of GeCl₄ with PBu₃. The adducts of PhGeCl₃ have larger enthalpies of formation than corresponding adducts of PhSnCl₃ (for example PhSnCl₃py₂, $\Delta H^0 = -139$, $K > 10^6$) but are of lower stability as is the case with the 1/1 adducts discussed above.

While the differences between the Lewis acidity of the organogermanium compounds and their tin analogues is understandable in terms of the smaller size of the germanium atom leading to increased bond strength and lower stability because of steric effects, the corresponding silicon compounds behave quite differently: the compounds R_{*n*}SiCl_{4-*n*} form addition compounds with 4-*n* molecules of base, even when *n* is small and the base is 1,10-phenanthroline; in all cases the adduct stabilities are very high and there is no evidence of steric restraints. This has been interpreted as an indication that the chlorine atoms act as Lewis acid centres in the silicon compounds, rather than the small, inaccessible silicon atom [13]. The present results, showing that even with the rather larger germanium atom access is beginning to be restricted so that the coordination number is often only five, give some support to the idea that the silicon atom in the organosilicon compounds may be quite inaccessible, so that the only possible Lewis acid sites are the chlorine atoms.

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