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Adducts of organogermanium and organotin chlorides with triphenylphosphine oxide and hexamethylphosphoramide

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Abstract

The acidities of several organogermanium and organotin chlorides toward the Lewis base hexamethylphosphoramide ($[(CH_3)_2N]_3PO$, HMPA) were determined by monitoring the ^{31}P chemical shifts of the base in equimolar mixtures with the acids. Similar calorimetric studies were made on the acidities of organogermanium chlorides toward triphenylphosphine oxide (TPPO). Previously reported calorimetric and NMR data for organotin chloride adduct formation with TPPO were used to show that HMPA is a stronger base than TPPO. Both NMR and calorimetric methods do not detect the formation of adducts by organogermanium compounds with the bases TPPO, HMPA, and DMSO.

Introduction

Although $GeCl_4$ is known to form both 1/1 and 1/2 adducts with monodentate bases [1], the Lewis acidity of organogermane halides has received little attention. We have previously reported that trimethylchlorogermane does not form an adduct with triphenylphosphine oxide (TPPO) [2], whereas Graddon and Rana [3] have found 1/1 and 1/2 adducts of $(CH_3)_2GeCl_2$ and $C_6H_5GeCl_3$ with several bases, including pyridine, pyridine-*N*-oxide, and tributylphosphine. For the formation of the 1/1 adduct of $(CH_3)_2GeCl_2$ with pyridine and the 1/2 adduct of $C_6H_5GeCl_3$ with pyridine equilibrium constants of 2 and 3×10^4, respectively, were reported [3]. Because of our surprise in finding such a dramatic difference in acidity between germanium and tin homologs, we have undertaken a more comprehensive study of their relative acidities. In order to be able to detect low equilibrium constants we chose to use hexamethylphosphoramide ($[(CH_3)_2N]_3PO$, HMPA) as one of the Lewis bases. HMPA has a donor number of 39 and according to this measure of basicity is one of the strongest monodentate bases (pyridine has a donor number of 33). The Lewis interactions were monitored by both ^{31}P NMR and calorimetry.

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Experimental

All operations were carried out under argon with P_2O_5 as desiccant. TPPO was vacuum dried and HMPA was distilled over CaO and stored over molecular sieves. Benzene was dried over sodium wire. Chlorobenzene and methylene chloride were distilled over P_2O_5 and stored over molecular sieves. Organotin halides were sublimed prior to use; organogermanium acids were in most cases found to be sufficiently pure to use directly as supplied by Alfa Chemical Co. (sealed under argon). In several cases, the organogermanium halides were also distilled as a check on purity and reproducibility of results. Purity was determined by ^1H and ^{13}C NMR and was found to be greater than 95%.

NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 36.19 MHz. Sample preparation and data analysis for both NMR and calorimetric studies have been previously described [4,5].

Results and discussion

Table 1 contains the equilibrium constants found for the complexes of several organotin halides with TPPO and HMPA in benzene or chlorobenzene at 25 °C. These constants were obtained from plots of the ^{31}P chemical shift of equimolar acid/base mixtures at six different concentrations. When the only equilibrium present in solution is formation of the 1/1 adduct, the plot of $\Delta_c[\delta_{\text{observed}} - \delta_{\text{base}}]$ vs. $\sqrt{\Delta/\text{conc}}$ is a straight line and the equilibrium constant is obtained from the slope of the line and the intercept [5]. The correlation coefficients for the plots were generally greater than 0.98 and, except for the plot for $(CH_3)_2SnCl_2$, were sufficiently linear to assume that formation of the 1/1 adducts predominate and to allow the calculation of approximate equilibrium constants for these adducts. The predominant formation of the 1/1 adducts is consistent with all of our previous work on mono, di, and trihalo systems [4,5]. The chemical shifts for $(CH_3)_2SnCl_2$ were essentially concentration independent, indicating the presence of only adduct in the mixtures with HMPA. Thus, the determination of an equilibrium constant for

Table 1

Equilibrium constants for formation of 1/1 adducts, 25 °C

	$TPPO_{NMR}$	$TPPO_{cal}$	$HMPA_{NMR}$	Solvent
$(CH_3)_3SnCl$	14	21.4	150	C_6H_6
			290	ClC_6H_5
			260	C_6H_{12}
			1	$CHCl_3$
$(CH_3CH_2)_3SnCl$	8	9.1		C_6H_6
			100	ClC_6H_5
$(CH_3CH_2)_3SnBr$	5	7.6		C_6H_6
			80	ClC_6H_5
$(CH_3)_2SnCl_2$	460	126		C_6H_6
			$>10^4$	ClC_6H_5
CH_3SnCl_3	7300	566		C_6H_6
			$>10^5$	ClC_6H_5

Table 2

Enthalpies of solution of organogermanium halides in benzene, kcal mol^{-1} 298 K

Compound	Enthalpy
$(CH_3)_3GeBr$	0.31 ± 0.02
$(CH_3)_3GeI$	0.27 ± 0.02
$(CH_3)_2GeCl_2$	0.04 ± 0.01
CH_3GeCl_3	-0.05 ± 0.01

this acid was impossible, but it can be estimated to be greater than 10^4. Also given in Table 1 are previously reported equilibrium constants determined by calorimetry. The large difference in K for CH_3SnCl_3 as obtained by calorimetry and NMR is a result of simultaneous 1/1 and 1/2 equilibria. Schematic mapping of a large number of calorimetry runs permitted the determination of a true K_1. A full analysis of the equilibria in the trihalide systems will be given in a later paper. It is obvious from the values in this table that HMPA is a considerably stronger base than TPPO toward these acids.

The dependence of the equilibrium constant on solvent was also explored for trimethyltin chloride. All plots were good straight lines and gave the following constants for the solvents: ClC_6H_5, 290; C_6H_6, 150; C_6H_{12}; 260; $CHCl_3$, 1. The low value for $CHCl_3$ can be rationalized by hydrogen bonding to free HMPA, which would stabilize the base more than the adduct. We await the results of a more complete solvent study before proposing a rationalization for the large value for chlorobenzene (relative to benzene and cyclohexane).

Because of our previous inability to detect acidity for trimethylchlorogermane, the ^{31}P chemical shifts of TPPO in equimolar (0.1 M) mixtures in benzene with the following germanes were observed: $(CH_3)_3GeBr$, $(C_6H_5)_2GeCl_2$, and CH_3GeCl_3. All of these compounds produced no change in the ^{31}P shift of the base. This observation was supported by calorimetry which showed no evolution of heat which could be attributed to adduct formation upon mixing the acids $(CH_3)_3GeBr$, $(CH_3)_3GeI$, $(CH_3)_2GeCl_2$, and CH_3GeCl_3 with TPPO. Thus, when a 0.01 M solution of acid was added to a 0.2 M solution of TPPO in benzene the heat of solution was the same as that observed in pure benzene. When DMSO was used as the base with $(CH_3)_2GeCl_2$ no heat beyond the heat of solution was observed. The enthalpies of solution of the germanes in benzene are given in Table 2.

Finally, the strongest available organogermanium acid, CH_3GeCl_3 was allowed to interact with the stronger base HMPA. Even with this acid/base pair no change in ^{31}P shift could be detected. Likewise, the heat of interaction of $C_2H_5GeCl_3$ with HMPA in benzene was zero, and in cyclohexane so small as to preclude determination of an equilibrium constant. The conclusion, therefore, is that organogermanium halides exhibit no detectable (by these methods) acidity toward even strong Lewis bases such as HMPA.

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