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The formation of organotin halide adducts with triethylphosphine oxide

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Abstract

The Lewis acid–base interactions of organotin mono-, di-, and tri-halides with triethylphosphine oxide (TEPO) were investigated by determining the ^{31}P chemical shift of equimolar mixtures of the acid and base in benzene. The concentration dependence of this shift was used to determine the equilibrium constant for formation of the 1/1 adduct. The acceptor number of the acid was obtained from the ^{31}P chemical shift of the adduct and by extrapolation of the ^{31}P shift to infinite dilution. Equilibrium constants for the complexes of the same acids with both TEPO and triphenylphosphine oxide (TPPO) were correlated by multiple regression analysis with these acceptor numbers (AN) and the molar refractivities (MR) of the acids. Enthalpy changes for the formation of adducts with TPPO were also found to correlate with AN and MR.

Introduction

Recent studies [1–3] have shown that organotin mono- and di-halides form predominantly 1/1 adducts in solution with a variety of monodentate bases. Preliminary results from our laboratory indicate that organotin trihalides also form 1/1 adducts, but that other species, including 1/2 adducts, are also formed with stronger bases. The equilibrium constants for the formation of the 1/1 adducts, and, in a few cases, the 1/2 adducts, with triphenylphosphine oxide and several other bases have also been reported [2,3].

Because of its use as the standard base for the definition of acceptor numbers [4], triethylphosphine oxide is a particularly interesting base for the study of Lewis interactions. Although acceptor numbers were originally defined for solvents by extrapolation of the ^{31}P chemical shift to infinite dilution in hexane (with the acceptor number of the $SbCl_5$ complex in dichloroethane arbitrarily set to 100), this concept can be extended to any Lewis acid. Accordingly, we have determined the

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^{31}P chemical shift of the Lewis base triethylphosphine oxide in the formation of adducts with organotin halides of the type: R_3SnCl, R_2SnCl_2, and $RSnCl_3$. The concentration dependence of the shift was used to determine four parameters: the equilibrium constants for the formation of the 1/1 adducts, the chemical shift of the 1/1 adduct, the acceptor number based on the shift of the 1/1 adduct, and the acceptor number derived from the ^{31}P shift at infinite dilution.

Experimental

All operations were carried out in an argon atmosphere. ACS reagent grade benzene was dried over sodium. Triethylphosphine oxide was sublimed under reduced pressure and stored under argon. Organotin halides were sublimed or distilled and were judged to be greater than 97% pure from their proton and ^{13}C NMR spectra.

Phosphorus-31 spectra were obtained on a JEOL FX-90Q spectrometer at 25 °C in 10 mm tubes. Stock solutions of acid and base, both 0.2 *M* in benzene, were prepared and then mixed equally by volume in a 10 ml volumetric flask. A 5-ml aliquot was in turn diluted to 10 ml, and this was repeated until six solutions, ranging in concentrations from 0.1 to 0.003125 *M* were prepared. The reference standard, trimethyl phosphate, dissolved in deuterioacetone in a 1/50 ratio was present in a coaxial tube. The equilibrium constant for formation of a 1/1 adduct can be obtained from the exchange-averaged chemical shift of the ^{31}P-containing species from the equation [5]:

$$\Delta = \Delta_c - (\Delta_c/K)^{1/3}(\Delta/C_0)^{1/2}$$

where Δ is the difference between the chemical shift of the solution and that of the base, Δ_c is the difference between the chemcial shift of the adduct and the free base, and C_0 is the initial concentration of the acid and base. The equilibrium constant is obtained from the slope of a plot of Δ vs. $(\Delta/C_0)^{1/2}$, while the chemical shift of the adduct is obtained from the intercept. Acceptor numbers are based on the ^{31}P shifts referenced to $(C_6H_5)_2POCl$, which has a shift of 41.29 ppm relative to trimethyl phosphate.

The calorimetric methods of data collection and the data analysis have been previously described for most of the systems of this study [1,2]. For the investigation of the adducts of methyl- and phenyl-tin trichlorides a different calorimeter was employed. A Parr Solution Calorimeter (Model 1451), modified for electrical calibration, was housed in a Vacuum Atmospheres HE-43-2 Dri Lab. All sample preparations and all calorimetric analyses were carried out in the Dri Lab so that a moisture-free atmosphere was maintained throughout the analysis.

Results and discussion

The plots of Δ vs. $(\Delta/C_0)^{1/2}$ were essentially straight lines for the mono- and di-halides with least squares correlation coefficients above 0.99, but the lines acquired a noticeable curvature (middle points lower) for the trihalides. However, the shifts for the trihalides did not vary much as the concentration changed over a 20-fold range, presumably because of the very high extent of complexation. The

Table 1

Chemical shifts, equilibrium constants and acceptor numbers

Compound	^{31}P shift [a]	K, 25 °C [b]	AN [c]	AN [d]
$(CH_3)_3SnCl$	4.53	1.0×10^2	11	26
$(CH_3CH_2)_3SnCl$	3.67	62	7	25
$(CH_3CH_2)_3SnBr$	3.54	38	8	27
$(n\text{-}C_4H_9)_3SnBr$	3.78	81	9	23
$(C_6H_5)_3SnCl$	6.87	1.7×10^2	16	37
$(CH_3)_2SnCl_2$	12.95	2.9×10^3	30	39
$(CH_3CH_2)_2SnCl_2$	11.93	2.2×10^3	28	37
$(n\text{-}C_4H_9)_2SnBr_2$	10.16	6.8×10^2	24	38
$(C_6H_5)_2SnCl_2$	17.91	1.0×10^4	42	47
CH_3SnCl_3	20.64	6.0×10^4	49	51
$C_6H_5SnCl_3$	27.34	1.0×10^6	64	65

[a] Relative to $(C_6H_5)_2POCl$, extrapolated to infinite dilution in 1/1 mixtures of acid and triethylphosphine oxide. [b] For formation of 1/1 adducts with triethylphosphine oxide. Estimated error in K is 10%. [c] Acceptor number determined from ^{31}P shift extrapolated to infinite dilution. [d] Acceptor number determined from shift of adduct as obtained from Δ vs. $(\Delta / C_0)^{1/2}$ line.

straight lines obtained are a good indication of predominant formation of the 1/1 complex. Computer simulations reveal that inclusion of the 1/2 equilibrium leads to curvature, the extent of which depends upon the relative values of K_1 and K_2, the equilibrium constants for the formation of 1/1 and 1/2 adducts, respectively [2].

Table 1 contains the equilibrium constants for the formation of the 1/1 adducts, the ^{31}P chemical shift of equimolar mixtures of acid and base extrapolated to infinite dilution, the acceptor number derived from the infinite dilution shift, and the acceptor number derived from the adduct shift using the equation of Gutmann [4].

The equilibrium constants are larger than those for the formation of the analogous triphenylphosphine oxide adducts [1,2] given in Table 2, as expected on the basis of the smaller size and greater electron-releasing effect of the ethyl group. The

Table 2

Equilibrium constants and ΔH for adduct formation with TPPO, and correlation parameters

Compound	K_{cal} [a]	K_{NMR} [a]	$-\Delta H$ [a]	AN	MR [b]
$(CH_3)_3SnCl$	21.4	14	8.1	26	23.0
$(C_2H_5)_3SnCl$	9.1	8	8.3	25	36.9
$(C_2H_5)_3SnBr$	7.6	5	8.7	27	39.8
$(C_6H_5)_3SnCl$	12.6	15	8.3	37	82.1
$(CH_3)_2SnCl_2$	126	460	9.3	39	23.4
$(C_2H_5)_2SnCl_2$	98	173	9.4	37	32.7
$(C_4H_9)_2SnBr_2$	40	33	8.6	38	56.9
$(C_6H_5)_2SnCl_2$	142	295	11.1	47	62.8
CH_3SnCl_3	566	7300	12.3	51	23.7
$C_6H_5SnCl_3$	4.3×10^4	2.3×10^4	13.3	65	43.5

[a] Data from references 1 and 2. Vide infra. [b] The molar refractivity was calculated by assuming additivity of the R groups and halogens. The contribution by Sn to MR was assumed to be the same for all acids and thus is not included in the calculation of MR.

constants also show the normal dependence on the number of halogens attached to tin, the trihalides having constants that, in fact, extend beyond the reliable range of this method. The other structural effect obvious from Table 1 is the greater acidity of the phenyl derivatives compared to the homologous alkyl derivatives. The constants have an associated error estimated to be about 10%.

The chemical shifts of the adducts as obtained from the Δ vs. $(\Delta/C_0)^{1/2}$ vary monotonically with the equilibrium constants. Thus, it appears that greater acidity as measured by the equilibrium constant is also accompanied by an interaction in the adduct that removes more electron density from the phosphorus, thereby presumably increasing the $1/r^3$ factor in the paramagnetic term for the chemical shift.

The acceptor number as originally defined by Gutmann for solvents used the infinite dilution shift of triethylphosphine oxide in the "acceptor" solvent. Because the observed shift is the weighted average of the shift of the free base and that of the adduct (plus any other ^{31}P-containing species present), this method ensures that the equilibrium is shifted to essentially complete formation of the triethylphosphine-solvent "adduct", and that the infinite dilution shift is therefore the shift of the "adduct".

In the present study, the infinite dilution shift of 1/1 mixtures of base and acceptor acid does not approximate the shift of the adduct, because the equilibrium is shifted more toward the free base as the concentration decreases. Nevertheless, the acceptor number derived from these infinite dilution shifts does correlate with the equilibrium constants of the acids. In order to obtain an acceptor number comparable to that defined by Gutmann, the chemical shift of the adduct (obtained from the Δ vs. $(\Delta/C_0)^{1/2}$ line) was used as the acceptor number. Because of the better correlations (vide infra) obtained with this set of acceptor numbers (AN), it was adopted as the better means of acceptor behavior. Addition of large excesses of acid to several solutions confirmed that these adduct shifts are indeed very close to the shift that would be obtained with the equilibrium shifted toward the adduct.

Table 2 contains previously reported [1,2] equilibrium constants determined by both calorimetric and NMR methods for adduct formation of these acids with triphenylphosphine oxide (TPPO) in benzene solvent, enthalpies calculated from calorimetric data, the acceptor number (AN), and molar refractivities, MR. The calorimetric and NMR results for diphenyltin dichloride were redetermined and the recent results are reported here. The methyl- and phenyl-tin trichloride data are reported for the first time and will be discussed in a later publication. Both the methyl- and phenyl-tin trichlorides form both 1/1 and 1/2 adducts in benzene solvent. The equilibrium constants and enthalpy changes given in Table 2 refer to the 1/1 adducts only.

Linear free energy relationships have been used to rationalize covalent and electrostatic effects on equilibrium constants and generally take the form [6]:

$$\log K = b\beta + s\pi + C$$

where β is a measure of the electron-donating ability of the base and π is a measure of the polarizability of the base. For the equilibria of this study, correlations using the electron-accepting ability of the acid as measured by the acceptor number (AN) and the polarizability of the acid measured by the molar refractivity (MR) as calculated by Hansch and Leo [7] were attempted.

Table 3

Regression Analyses[a] $XYZ = XYZ^{\circ} + a\mathrm{AN} + b\mathrm{MR}$

XYZ	XYZ°	a	b	R	SE
$\log K_{\mathrm{NMR}}$ [b]	-0.773	0.0974	-0.0222	0.990	0.20
$\log K_{\mathrm{NMR}}$ [c]	-0.417	0.105	-0.0107	0.979	0.32
$\log K_{\mathrm{cal}}$ [d]	-0.807	0.0867	-0.0151	0.973	0.29
ΔH [d]	-5.088	-0.141	$+0.0209$	0.957	0.61

[a] R = multiple correlation coefficient; SE = standard error of estimate. [b] K for adducts with TPPO determined from NMR data. [c] K for adducts with TEPO determined from NMR data. [d] K, ΔH for adducts with TPPO determined from calorimetric analysis; ΔH in kcal mol^{-1}; in benzene at 298 K

Although regressions with AN alone resulted in correlation coefficients above 0.92, dual regressions with AN and MR were judged superior according to the statistical criterion given by Ehrenson [8]. Thus, all dual regression equations given in Table 3 are at the 95% confidence level or greater. Correlations were also attempted using AN and the dipole moment of the acid but were not found to be as good as those with AN and MR.

The regression equation for log K contains a positive coefficient for the AN term, indicating that as the electron accepting ability of the acid increases, log K increases. The coefficient for MR, on the other hand, is negative, indicating that the contribution of the polarizability of the acid to adduct formation is destabilizing. This is probably a result of the increased acid-solvent interactions which shift the equilibrium to the free acid and base as the polarizability of the acid increases.

The regression equation for enthalpy shows that ΔH is also correlated with AN and MR, although the coefficient of correlation is not as high. The negative sign of the AN coefficient means that the enthalpy becomes more negative (more favorable to adduct formation) as the acceptor number increases. The positive sign for the polarizability term can be explained by the increased difficulty of removing solvent molecules from the solvation shell of the acid, thereby producing an unfavorable enthalpy change, as the polarizability of the acid increases.

Correlations between entropy and AN, dipole moment, or MR were found to be poor. This is largely a result of the sensitivity of ΔS to errors in ΔH and ΔG from which it is calculated.

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