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The formation of organotin halide adducts with 1,2-bis(diphenylphosphine oxy)ethane and methyldiphenylphosphine oxide

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Abstract

The acidities of a series of organotin halides toward the bidentate base 1,2-bis(diphenylphosphine oxy)ethane ($[(C_6H_5)_2P(O)CH_2]_2$, EDPO) were determined by monitoring the ^{31}P chemical shift of equimolar mixtures of acid and base as a function of concentration in chloroform. Additional studies used the analogous Lewis monodentate base methyldiphenylphosphine oxide (MPPO) and the Lewis base triphenylphosphine oxide (TPPO). In all cases, formation of a 1/1 adduct was found to predominate. Comparison of the equilibrium constants for specific organotin halides showed that EDPO and MPPO have comparable base strengths in chloroform. TPPO is a weaker base than either EDPO or MPPO in chloroform. Tin-119 NMR indicated that the organotin halide-EDPO adducts have 5-coordination at tin with no chelation of the base.

Introduction

Previous studies have shown that the monodentate bases TPPO and triethylphosphine oxide form predominantly 1/1 adducts with triorganotin halides, diorganotin dihalides, and organotin trihalides in solution [1,2]. Studies of adduct formation with organotin halides, particularly dimethyltin dichloride, and bidentate bases have produced evidence for both chelated 1/1 6-coordinate adducts and adducts that utilize the bidentate base as a bridge rather than as a chelate [3]. Because the phosphine oxide system provides a convenient vehicle (due to the relatively high basicity and the abundance of a nucleus with a high nuclear receptivity) for the study of Lewis interactions, the present study was undertaken to determine the stoichiometry and equilibrium constants for adduct formation between a bidentate phosphine oxide and organotin halides in solution.

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Experimental

All operations were carried out in an argon atmosphere using oven-dried glassware. All organotin halides and the bases were obtained commercially. Organotin halide solids were purified by vacuum sublimation and organotin halide liquids were purified by vacuum distillation. The phosphine oxides were dried in a vacuum desiccator over Drierite for approximately 12 h. Melting points for vacuum dried TPPO and EDPO were identical to the melting points of the sublimed reagents and in good agreement with literature values [4,5]. Chloroform was dried over activated alumina and then stored over Linde Type 4-A molecular sieves for no more than 3 days. Sample preparation and data analysis have been previously described [1,2]. The shift of the free base used in the least squares analyses was an average over the concentration range 0.1–0.01 *M*. The difference in shift of the EDPO over this range was 0.2 ppm.

Results and discussion

Table 1 contains the equilibrium constants for the formation of adducts of several organotin halides with EDPO, MPPO, and TPPO in chloroform at 25 °C. These constants were obtained from plots of the ^{31}P chemical shift of equimolar acid–base mixtures of 5 or 6 different concentrations. When the only equilibrium in solution is formation of the 1/1 adduct, the plot of delta (observed shift–base shift) vs. the square root of delta/concentration is a straight line and the equilibrium constant is obtained from the slope of the line and the intercept [1,2].

The correlation coefficients (r) for the EDPO plots were greater than 0.95 with the following exceptions: $(C_6H_5)_3SnCl$-EDPO, $r = 0.74$ and $(CH_3)_2SnCl_2$-EDPO, $r = 0.67$. The correlation coefficients for the MPPO plots were greater than 0.99 with the following exception: $(CH_3)_3SnCl$/MPPO, $r = 0.87$. The correlation coefficients for the TPPO plots were greater than 0.99. All deviations from straight lines can be attributed to the formation of small amounts of 1/2 adducts or association with solvent (vide infra). For those systems that produced high correlation coefficients the associated error in K is typically 10%; obviously, larger deviations from

Table 1

Equilibrium constants for the formation of 1/1 adducts in chloroform at 25 °C [a]

Acid	(EDPO)	(MPPO)	(TPPO)
$(CH_3)_3SnCl$	<1	5×10	<1
$(C_6H_5)_3SnCl$	8×10^2		
$(CH_3)_2SnCl_2$	2×10^2	3×10^2	1×10^2
$(C_3H_7)_2SnCl_2$	5×10	5×10	
$(C_4H_9)_2SnBr_2$	2×10		
$(C_4H_9)_2SnCl_2$	8×10	6×10	4×10
CH_3SnCl_3	3×10^3	8×10^3	4×10^3
$C_4H_9SnCl_3$	3×10^3		
$C_6H_5SnCl_3$	2×10^3		

[a] Errors estimated at ca. 10% except for $(C_6H_5)_3SnCl$/EDPO (60%), $(CH_3)_2SnCl_2$/EDPO (76%), and $(CH_3)_3SnCl$/MPPO (33%).

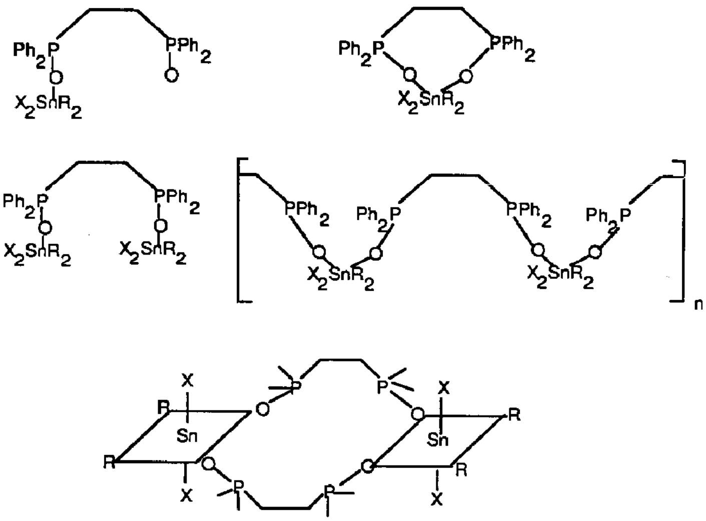

Fig. 1. Structures for the EDPO adducts.

linearity, attributable to additional equilibria, result in correspondingly larger errors.

Chloroform was chosen as the solvent for all systems due to the insolubility of EDPO in other solvents. That this solvent preferentially interacts with the free base, presumably by hydrogen-bonding, is revealed by the uniformly lower constants obtained for the TPPO adducts of $(CH_3)_2SnCl_2$, $(C_4H_9)_2SnCl_2$, and CH_3SnCl_3 in $CHCl_3$, and by the temperature dependence of the chemical shift of the EDPO (31.00 ppm at 25 ° C, 31.63 at -20 ° C). The equilibrium constants for these systems in benzene are 5×10^2, 1×10^2, and 7×10^3, respectively; in $CHCl_3$ the constants are 1×10^2, 4×10, and 4×10^3, respectively. Schematic mapping analysis (described previously [1]) for several systems with 10 to 12 concentrations showed that data are best fit by either formation of the 1/1 adduct or by simultaneous formation of 1/1 adduct and solvent association with the base.

Five structures can be predicted for the organotin halide/EDPO adducts (see Fig. 1): a 1/1 adduct with 5-coordination at tin, a chelated 1/1 adduct with 6-coordination at tin, a 2/1 adduct with 5-coordination at each tin, a 1/1 polymer adduct, and a 1/1 associated adduct with 6-coordination at each tin.

The coordination number at tin was established from the ^{119}Sn chemical shifts of the $(C_3H_7)_2SnCl_2$ adducts of MPPO and EDPO. The tin shift is known to be sensitive to coordination number in systems where the adduct predominates; i.e., K is large or the equilibrium is forced to the adduct with excess base. For example, the ^{119}Sn shift of the 1/1 adduct of $(CH_3)_3SnCl$/DMSO has been reported as 3 ppm, while the 1/2 adduct (in excess DMSO) has a reported ^{119}Sn shift of -246 ppm. The monodentate base MPPO provides an excellent model for the determination of coordination number, especially since it forms 1/1 adducts with most of the acids studied. With $(C_3H_7)_2SnCl_2$, an excellent straight line was obtained for the ^{31}P plot and, moreover, the equilibrium constant for the formation of this adduct is sufficiently high to insure that most of the base is complexed to the adduct at a concentration of 0.1 M. The ^{119}Sn shifts of this complex and that of the EDPO analog at 0.1 M were -35.3 ppm and -30.4 ppm, respectively. The similarity of the shift of the adducts indicates that organotin halide/EDPO adducts have 5-coordinate tin centers. Thus, organotin halides predominantly form 1/1 adducts with 5-coordination at tin and no chelation of the bidentate base. This conclusion is in agreement with the 1/1 structure found by X-ray diffraction for the EDPO adduct of $(C_6H_5)_3SnCl$ [6] and the 1/1 polymeric structure (bridging EDPO) of the EDPO adduct of $(C_4H_9)_2SnCl_2$ [7]. The solid state structure of the former is 5-coordinate, while the latter is a distorted tetragonal pyramid with a more loosely bonded oxygen from another EDPO occupying a sixth site. In solution this loosely associated species is probably more likely to dissociate to 5-coordinate species.

Most of the same trends in Lewis acidity previously observed [1,2] are shown by the EDPO adducts. The dihalides are generally stronger acids than the monohalides; the trihalides are the strongest organometallic tin acids. Except for the butyl derivative the acidities of the dialkyltin dichlorides decrease with an increase in size of the alkyl group, and, at least for the monohalides, the phenyl group confers increased acidity (the diphenyltin dichloride adduct was insoluble). Comparison of the equilibrium constants for specific organotin halides showed that EDPO and MPPO have comparable base strengths in chloroform. TPPO is a weaker base than either EDPO or MPPO in chloroform.

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