Journal of Organometallic Chemistry, 385 (1990) 33–37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20549

The Lewis acidities of organotin halides toward tributylphosphine and tributylphosphine oxide: the effect of the donor site

Claude H. Yoder, Julie C. Otter, Alex Grushow, Travis F. Ganunis, Belinda G. Enders, Abrahim I. Zafar and J.N. Spencer

Department of Chemistry, Franklin and Marshall College, Lancaster, PA 17604 (U.S.A.)

(Received September 7th, 1989)

Abstract

The stoichiometry of the adducts formed by tributylphosphine (TBP) and tributylphosphine oxide (TBPO) with organotin halides in benzene was determined by ^{31}P NMR spectroscopy and by calorimetry. Except for two cases, all adducts were found to have 1/1 stoichiometry. For the $MeSnCl_3$/TBP and the Me_2SnCl_2/TBPO systems there was evidence for a small amount of 1/2 adduct. Both techniques indicate no adduct formation between triorganotin halides and TBP, whereas the equilibrium constants for the 1/1 adducts of TBPO with triorganotin halides range from 150 to 300. With the diorgano- and monoorgano-tin halides, however, the equilibrium constants for 1/1 adduct formation with TBP are the same as or greater than those for TBPO. Enthalpy changes determined by calorimetry show the same reversal of basicity, which can be attributed to steric repulsions in the weakly acidic triorgano derivatives with TBP. These repulsions are overwhelmed by the greater intrinsic tin–phosphorus dative bond strength in the di- and mono-organotin halide adducts.

Introduction

Our previous work on the Lewis acidities of model organotin halides has revealed predominant 1/1 stoichiometry for monodentate bases such as triphenylphosphine oxide (TPPO), triethylphosphine oxide (TEPO), DMSO, pyridine *N*-oxide, and acetonitrile [1,2]. Even the bidentate base 1,2-bis(diphenylphosphoryl)ethane ($[(C_6H_5)_2P(O)CH_2]_2$, EDPO) forms monodentate 1/1 adducts in $CHCl_3$ solution [3]. These bases all contain a hard basic site—either oxygen or nitrogen. Our present study is devoted to the effects of a soft basic site on the stoichiometry and relative acidities of these model organotin acids. Although not strictly isostructural with the phosphine oxides previously studied, tributylphosphine is structurally analogous to

0022-328X/90/$03.50

the $(C_4H_9)_3P$ moiety of TBPO, contains a sensitive, magnetically-active nucleus, has one soft basic site, is relatively easy to dry and purify (although precautions must be taken to prevent oxide formation), and is a moderately good Lewis base toward organotin halides.

Experimental

Reagents. Tributylphosphine was obtained from Aldrich Chemical Co. in 98% purity and checked for the presence of TBPO by ^{31}P NMR spectroscopy. In most cases it was vacuum distilled and then stored over molecular sieves. In several cases the purity was considered sufficiently high to use directly as obtained from Aldrich. The TBP was stored under Ar and constantly checked for oxidation. TBPO was purified by vacuum sublimation. The organotin acids were purified by vacuum sublimation or distillation. Purity was checked by proton, ^{13}C, and ^{119}Sn NMR spectra and melting points, and in all cases was believed to be greater than 98%. Benzene was dried over sodium and stored over molecular sieves. All operations were performed under an argon atmosphere using ovendried glassware.

Calorimetry. The Parr solution calorimeter Model 1451 thermistor bridge was utilized for the detection of temperature changes. The calorimeter was housed in an HE-43-2 DriLab constructed by Vacuum Atmospheres. The DriLab contained the calorimeter, a balance, and all necessary reagents so that the entire analysis from solution preparation to data collection could be carried out in a dry atmosphere. The analysis was carried out by a batchwise technique. A base was injected into a 100 ml solution of the acid in benzene which was contained in the reaction vessel. Usually a series of 10 successive injections of the base was made into the acid solution. After each injection an electrical calibration was carried out so that the heat resulting from each injection could be calculated. Then a new solution of acid of another concentration was prepared and the injection process repeated. The concentration of the acid solutions ranged from 0.01 to 0.1 *M* and the concentration of the base ranged from 0.002 to 0.15 *M*. The enthalpy of solution at infinite dilution of TBP in benzene was 1.14 ± 0.05 kcal/mol.

The schematic mapping techniques used for data analysis have been previously described [1,2].

NMR analyses. Preparation of solutions and determination of equilibrium constants have been previously described [1,2].

Results and discussion

Schematic mapping of the calorimetry results indicated that in all but two cases analyzed by calorimetry the data were well fit by the presence of only the 1/1 adduct in solution. For the interaction of TBP with $MeSnCl_3$, two equilibria, formation of both 1/1 and 1/2 adducts, gave the best fit. The addition of the first mole of TBP produced the values of $K_1 \geq 10^5$ and $\Delta H_1 = -17.5 \pm 0.5$ kcal/mol; the addition of the second mole of TBP gave values of $K_2 = 20 \pm 3$, $\Delta H_2 = -16 \pm 2$ kcal/mol. For the interaction of TBPO with Me_2SnCl_2, schematic mapping produced a somewhat unsatisfactory fit for the formation of only the 1/1 adduct, and a second equilibrium, probably formation of the 1/2 adduct, is likely. The schematic mapping solution for simultaneous formation of the 1/1 and 1/2 adducts gave the

Table 1

Equilibrium constants for the formation of 1/1 adducts [a]

Compound	TBP	TBPO	TEPO	TPPO
Me_3SnCl	0	1.6×10^2	1.2×10^2	14
Ph_3SnCl	0	2.9×10^2	1.7×10^2	15
Pr_3SnCl	0			10
Et_3SnBr	0		38	5
Bu_3SnBr	0			
Me_2SnCl_2	9.1×10^2	6.0×10^3	2.9×10^3	4.6×10^2
Pr_2SnCl_2	5.6×10^2			1.0×10^2
Bu_2SnCl_2	3.1×10^2			1.2×10^2
Ph_2SnCl_2	$4\ \times10^4$	3×10^4	1×10^4	2.9×10^2
Bu_2SnBr_2	2.3×10^2		6.8×10^2	33
$MeSnCl_3$	$1\ \times10^5$	6×10^4	6×10^4	7×10^3
$BuSnCl_3$	4×10^4			

[a] Determined by NMR at $25\pm2°$ C; errors estimated at 10%.

values of $K_1 \geq 2000$, $\Delta H_1 = -13\pm1$ kcal/mole, $K_2 = 2\pm1$, $\Delta H_2 = -12\pm2$ kcal/mol.

The ^{31}P spectra of all complexes exhibited one resonance at higher frequencies than the free base. Several attempts to resolve these weighted average peaks at lower temperatures (to $-70\,°C$) were unsuccessful. Most of the $\Delta\nu$ vs $\sqrt{(\Delta\nu/\text{conc})}$ plots obtained from the ^{31}P NMR studies for TBP gave the good straight line plots (except for those of the triorganotin halides which showed no change in chemical shift as a function of concentration) expected for predominant formation of 1/1 adducts. The $MeSnCl_3$ plot, however, had considerable downward curvature (middle points low), as expected for the presence of some 1/2 adduct. The plots for TBPO had reasonably high correlation coefficients of 0.97 and higher, but all had slight downward curvatures, probably indicative of small amounts of 1/2 adduct. The slope and intercept of the plots were used to obtain the 1/1 equilibrium constants as described previously [1,2]. These values along with those previously obtained for triethylphosphine oxide (TEPO) and triphenylphosphine oxide (TPPO) are shown in Table 1, while calorimetric and NMR data are given in Table 2. The agreement between the values obtained by NMR and calorimetry is excellent. The equilibrium constants for the TBP adducts also agree with those reported previously by Farhangi and Graddon [4].

The data of Table 1 show a clear increase in equilibrium constants from TPPO to TBPO as expected due to the electronic effect of the groups attached to phosphorus. The data of Table 2 show that the enthalpy of interaction of TBP, TBPO, and TPPO with the organotin compounds increases with increasing number of halogens. These data also clearly illustrate that the enthalpy of interaction for TBP with the di- and tri-halides is more exothermic than for the same complexes with TPPO. It is clear from the data of Tables 1 and 2 that TBP is less basic than both TBPO and TPPO toward triorganotin halides.

The greater basicity of TBP toward the mono- and di-organotin halides is indicative of an inherently greater tin-donor bond strength in the phosphorus adducts. The lower basicity of the phosphine toward the triorganotin halides can be attributed to steric repulsions between the butyl groups of the TBP and the

Table 2

Thermodynamic parameters for R_nSnX_{4-n} adducts in benzene solvent (298 K) derived from calorimetric and NMR analysis

	K	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (cal mol^{-1} K^{-1})
Base: TPPO			
Me_3SnCl [a]	21.4 ± 0.5	8.1 ± 0.1	21
	14[f]	–	–
Et_3SnCl [a]	9.1 ± 0.4	8.3 ± 0.2	23
	14[f]		
Me_2SnCl_2 [b]	126 ± 19	9.3 ± 0.1	22
	4.6×10^{2} [f]	8.8 ± 0.4 [c]	17
Bu_2SnCl_2 [b]	118 ± 13	9.2 ± 0.1	21
	1.2×10^{2} [f]	–	–
$MeSnCl_3$ [d]	566 ± 85	12 ± 1	28
	7×10^{3} [f]	–	–
$PhSnCl_3$ [d]	4.3×10^{4}	13.3 ± 0.5	23
	2×10^{4} [f]	–	–
Base: TBPO			
Me_3SnCl	156 ± 10	9.4 ± 0.1	22
	1.6×10^{2} [f]	–	–
Me_2SnCl_2	$K_1: \geq 2000$	13 ± 1	< 28
	$K_2: 2 \pm 1$	12 ± 2	39
	$K_1: 6.0 \times 10^{3}$ [f]		
Base: TBP			
Me_3SnCl	0		
Ph_3SnCl	0		
Bu_3SnBr	0	–	–
Bu_3SnCl	0	–	–
Ph_3SnCl [e]	0	–	–
Bu_2SnCl_2	293 ± 28	13.6 ± 0.1	34.3
	3.1×10^{2} [f]	–	–
	322 ± 17 [e]	13.1 ± 0.2 [e]	31.8 [e]
Me_2SnCl_2	926 ± 217	14.5 ± 0.1	35.1
	9.1×10^{2} [f]	–	–
	1002 ± 60 [e]	12.9 ± 0.4 [e]	28.9 [e]
Ph_2SnCl_2	$2.9 \pm 0.4 \times 10^{4}$	18.5 ± 0.1	42
	4×10^{4} [f]		
	1.9×10^{4} [e]	17.6 [e]	38.5 [e]
$MeSnCl_3$	$K_1: \geq 10^{5}$	17.5 ± 0.5	< 36
	$K_2: 20 \pm 3$	16 ± 2	48
	$K_1: 1 \times 10^{5}$ [f]		
$BuSnCl_3$ [e]	2×10^{4}	22.1 ± 0.1	53.1
$PhSnCl_3$ [e]	$K_1: > 10^{5}$	22.5 ± 0.1	< 51
	$K_2: 2420 \pm 100$	17.9 ± 0.4	43.2

[a] Ref. 6. [b] Ref. 1. [c] Calculated from a combination of NMR and calorimetric data. See ref. *d*. [d] Ref. 2. [e] Ref. 4. [f] Determined by NMR.

substituents on tin. Examination of space-filling models confirms the presence of much more severe steric interactions in the phosphine adducts relative to the phosphine-oxide adducts. These steric repulsions are also present in the di- and mono-organo adducts but are overwhelmed by the greater Sn–P dative bond strength.

Assuming similar hybridization for the TBP and TBPO adducts, similar solvation changes for the formation of both adducts, and a less favorable entropy change for the formation of the TBP adduct due to restricted motion of the butyl groups (a result of steric interactions), the explanation for the greater basicity of TBP must lie in the interactions between the acid and base in the adduct. The postulation of an Sn–P dative bond that is inherently stronger than the Sn–O dative bond runs contrary to expectations based on the hard-soft acid–base principle and generally accepted trends in bond energies. Vibrational frequencies in a variety of tin tetrahalide adducts have also been rationalized in terms of soft behavior at the tin site [5]. Dispersion interactions between the polarizable butyl groups in proximity to alkyl and halo groups on the tin (and the tin itself) could also contribute to the greater basicity, but, clearly, if this were the only interaction of significance TBP would also be a stronger base toward the triorganotin halides.

Finally, the previously observed trends in acidity also hold for TBP and TBPO. An increase in size of the alkyl groups lowers the equilibrium constant; the phenyl group enhances the equilibrium constant relative to alkyl groups; and the equilibrium constant increases trihalo > dihalo > monohalo.

Acknowledgements

The authors are indebted to the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References

1 C.H. Yoder, D. Mokrynka, S.M. Coley, J.C. Otter, R.E. Haines, A. Grushow, L.J. Ansel, J.W. Hovick, J. Mikus, M.A. Shermak, and J.N. Spencer, Organometallics, 6 (1987) 1679.

2 J.N. Spencer, B.G. Enders, A. Grushow, S.P. Kneizys, W.L. Nachlis, D. Mokrynka, S.M. Coley, J.C. Otter, and C.H. Yoder, J. Organomet. Chem., 362 (1989) 53.

3 C.H. Yoder, S.M. Coley, S.P. Kneizys, and J.N. Spencer, J. Organomet. Chem., 362 (1989) 59.

4 Y. Farhangi and D.P. Graddon, J. Organomet. Chem., 87 (1975) 67.

5 M.F. Farona, Inorg. Chem., 14 (1975) 2020.

6 J.N. Spencer, R.B. Belser, S.R. Moyer, R.E. Haines, M.A. DiStravolo, C.H. Yoder, Organometallics, 5 (1986) 118.