Journal of Organometallic Chemistry, 362 (1989) 53-58
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The stoichiometry of organotin trihalides in solution

J.N. Spencer, Belinda G. Enders, Alexander Grushow, Steven P. Kneizys, Warren L. Nachlis, Dian Mokrynka, Suzanne M. Coley, Julie C. Otter, and Claude H. Yoder

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

(Received July 1st, 1988)

Abstract

The formation of Lewis acid–base adducts of the organotin trihalides, CH_3SnCl_3, $C_4H_9SnCl_3$, and $C_6H_5SnCl_3$, with acetonitrile, DMA, triphenylphosphine oxide (TPPO), and triethylphosphine oxide (TEPO) were studied by calorimetry and NMR spectroscopy. Schematic mapping of the calorimetry results for the TPPO adducts in benzene showed that the data are best fit by the assumption of simultaneous formation of 1/1 and 1/2 adducts. For the $C_6H_5SnCl_3$-TPPO system $K_1 = 4.3 \times 10^4$, $K_2 = 55$, $\Delta H_1 = -13.3$ kcal/mol, and $\Delta H_2 = -10.8$ kcal/mol. These equilibrium constants correspond to 93% 1/1 adduct and 3% 1/2 adduct at equilibrium after the acid and base are mixed in equimolar (0.1 M) concentrations. Thus, for this system and all others studied the 1/1 adduct predominates. Equilibrium constants for the formation of the 1/1 adducts were determined by ^{119}Sn or ^{31}P NMR spectroscopy from the shifts obtained in a series of equimolar mixtures of acid and base. These constants vary from approximately 1 for the acetonitile adducts to greater than 10^5 for TEPO and reveal the expected basicity order TEPO > TPPO > DMA > acetonitile.

Introduction

The many literature reports of 1/2 adduct formation for organo group 14 halides, particularly organotin halides, have popularized sp^3d^2 hybridization and octahedral complexes for main group Lewis acids [1]. Recently, however, there have been several reports of predominant formation of 1/1 adducts of these acids [2,4], including our own studies of the mono- [5,6] and dihalides [7]. Some of these adducts do obtain 6-coordination by association, at least in the solid state [8]. We report here our investigation of adduct formation with the strongest organotin halides, the trihalides, by calorimetry and ^{31}P and ^{119}Sn NMR spectroscopy. Our objectives were to determine the stoichiometry of the adducts in solution and its dependence on base strength, and the equilibrium constants and enthalpies for the formation of the adducts.

Experimental

Reagents. All organotin reagents were obtained commercially, and purified by either vacuum distillation or by sublimation under vacuum. 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%. TPPO and TEPO were sublimed in vacuo and stored in a vacuum desiccator. Acetonitrile, and dimethylacetamide were refluxed over CaH_2 for 12 h and then distilled. Chlorobenzene and CH_2Cl_2 were dried over $CaSO_4$, distilled from P_2O_5, and stored over molecular sieves. Benzene was refluxed over P_2O_5 for the calorimetry studies and treated with sodium ribbon for the NMR studies. All operations were performed under argon in a glove bag or drybox using oven-dried 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 batch-wise technique. A solution of the base in benzene was injected into a 100 ml solution of the acid in benzene which was contained in the reaction vessel. A series of usually 10 successive injections of the base solution 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 concentration of acid was utilized and the injection process repeated. The concentration of the CH_3SnCl_3 solutions ranged from 0.01 to 0.1 *M* and the concentration of TPPO in this series of experiments ranged from 0.002 to 0.15 *M*. A total of 45 data points were collected. The $C_6H_5SnCl_3$ concentrations ranged from 0.01 to 0.04 *M* while the TPPO equilibrium mixture concentrations were 0.002 to 0.2 *M*. For this system 35 data points were collected. A 0.25 *M* solution of TPPO in benzene was prepared and injected into benzene in order to detect and correct for any heat produced by the addition of the base. No heat was detected. The absence of heat in this procedure indicates that no self association of TPPO occurs in these analyses.

For the study of adduct formation of $C_4H_9SnCl_3$ and CH_3SnCl_3 with CH_3CN, pure CH_3CN was injected into benzene solutions containing 0.05 to 0.20 *M* acid. No appreciable self association of CH_3CN was detected over the concentration range 0.05 to 0.20 *M*. The enthalpy of solution at infinite dilution of CH_3CN in benzene was found to be 0.41 ± 0.01 kcal/mol. Analysis of the DMA/$C_4H_9SnCl_3$ was carried out similarly. The enthalpy of solution of DMA at infinite dilution in benzene is 0.014 ± 0.003 kcal/mol.

The analysis of the data has been previously described [5–7]. The schematic mapping program used is similar to those described by Abraham [9] and by Mullens [10]. The estimated errors in K_1 and K_2 are $\pm 15\%$ and the estimated uncertainties in ΔH_1 and ΔH_2 are ± 1 kcal/mol.

NMR studies. The preparation of solutions and the NMR acquisition parameters have been previously described [7].

Results and discussion

Calorimetric studies. The results of the analysis of the calorimetric data of the 35 data points for the $C_6H_5SnCl_3$/TPPO system are given in Table 1. The smallest error square sum (0.554) and hence the best fit for any model was obtained for simultaneous formation of 1/1 and 1/2 adducts. Error square sums for 1/1, 1/2, 2/1, simultaneous 1/1 and associated adduct, or simultaneous 1/1 and associated acid were much larger and indicate an incorrect model for the equilibria. Only in the case of simultaneous 1/1 and 2/1 complex formation was an error square sum (7.16) found which did not result in immediate rejection of the model. In this case an enthalpy change for the addition of a second acid molecule to the base has an unrealistic positive value of 19.0 kcal/mol. Because base association was eliminated experimentally (vide supra) the best fit of the calorimetric data is provided by simultaneous formation of 1/1 and 1/2 adducts. The relative values of the equilibrium constants are such that in an equimolar (0.1 M) mixture of acid and base, the 1/1 adduct predominates to the extent that only 3% of the base exists in the form of the 1/2 complex.

Schematic mapping of the 45 points of the CH_3SnCl_3/TPPO system gave error square sums that were not as good, but again the only reasonable model was simultaneous formation of 1/1 and 1/2 adducts (ESS = 7.71). The best values for this system are $K_1 = 566$, $K_2 = 21$ with an estimated uncertainty of 15%, $\Delta H_1 = -12.3$ kcal/mol and $\Delta H_2 = -13.9$ kcal/mol with an estimated uncertainty of ± 1 kcal/mol. Analysis of the butyltin trichloride and methyltin trichloride-acetonitrile systems in benzene gave the best fit with formation of only 1/1 adduct. For the former system $K = 1.4 \pm 0.4$ and $\Delta H = -2.8 \pm 0.8$ kcal/mol, while for the latter $K = 1.5 \pm 0.7$ and $\Delta H = -3.1 \pm 1.5$ kcal/mol. Likewise, the DMA/$C_4H_9SnCl_3$ system gave the best fit for a 1/1 adduct with $K = 812 \pm 124$ and $\Delta H = -10.6$ kcal/mol. The fit of the data in this case was not as good and suggests the possibility of a competing equilibrium.

NMR studies. The acetonitrile and DMA systems were investigated with ^{119}Sn NMR using chlorobenzene as solvent (except for $C_4H_9SnCl_3$/DMA which was

Table 1

Schematic mapping analysis of calorimetric data for phenyltin trichloride-TPPO system in benzene (35 points)

Model		K	ΔH (kcal/mol)	ESS [a]
1	1/1 adduct	307	-17.9	107
2	1/2 adduct	7.7×10^5	-24.8	74
3	2/1 adduct	1×10^{30}	-16.4	953
4	1/1 and 1/2 adducts	$K_1 = 4.3\times10^4$ $K_2 = 55$	$\Delta H_1 = -13.3$ $\Delta H_2 = -10.8$	0.554
5	1/1 and 2/1 adducts	$K_1 = 336$ $K_2 = 58$	$\Delta H_1 = -23.9$ $\Delta H_2 = +19.0$	7.2
6	1/1, associated acid	$K_1 = 9\times10^7$ $K_a = 2\times10^{13}$	$\Delta H_1 = -2\times10^9$ $\Delta H_a = -4\times10^9$	33
7	1/1, associated adduct	$K_1 = 938$ $K_a = 2\times10^{-6}$	$\Delta H_1 = -14.4$ $\Delta H_a = -6\times10^{16}$	178

[a] Error sum of squares.

Table 2

Equilibrium constants for 1/1 adduct formation [a]

Base	CH_3SnCl_3		$C_4H_9SnCl_3$		$C_6H_5SnCl_3$	
	NMR [a]	CAL [b]	NMR [a]	CAL [b]	NMR [a]	CAL [b]
CH_3CN	2	1.5	1	1.4	1	–
DMA	1×10^3	–	5×10^2	8×10^2	–	–
TPPO	7×10^3	566	5×10^3	–	2×10^4	4.3×10^4
TEPO	7×10^4	–	–	–	7×10^5	–

[a] Determined by ^{119}Sn or ^{31}P NMR. See experimental section for solvents, 25 °C. [b] The solvent for all calorimetric analyses was benzene.

done in CH_2Cl_2 because of the insolubility of the adduct in chlorobenzene), while the TPPO and TEPO systems were studied with ^{31}P NMR using benzene as solvent. All systems at all concentrations showed only one resonance for ^{119}Sn and/or ^{31}P as a result of rapid exchange of the base between all base-containing species in solution. The plots of δ_c vs. sqr(δ_c/conc) (δ_c = observed shift free base/acid shift) were reasonably good straight lines with correlation coefficients of 0.99 and higher for acetonitrile and DMA. Thus, for these bases the predominance of the 1/1 adduct can be assumed.

The TPPO systems were observed with both ^{119}Sn and ^{31}P NMR in concentration ranges of 0.8 to 0.03 *M* and 0.1 to 0.003 *M*, respectively. For both nuclei the shifts showed only a small variation with concentration, and the resulting curves had slight downward curvatures. Calculations of the weighted average chemical shift at a series of concentrations for various values of equilibrium constants and chemical shifts showed that usually simultaneous formation of 1/1 and 1/2 adducts produces upward curvature, but that if K_2 is small (and K_1 large) the curvature is in the observed direction. This type of curvature is also obtained for associated adduct, previously proposed form NMR studies [7] and observed in the solid state [8]. For the TEPO systems there was considerable downward curvature, indicative of the presence of larger amounts of another species, either 1/2 adduct or associated 1/1 adduct.

The equilibrium constants calculated from the least squares lines of the δ_c vs. sqr(δ_c/conc) are given in Table 2. These constants are calculated on the assumption that the primary species in solution is the 1/1 adduct and are probably good to within 10% for acetonitrile and DMA. For TPPO and TEPO, where another equilibrium is present, the associated error is larger. Nevertheless, the relative values of K_1 clearly show that (a) the trihalides are the strongest organotin Lewis acids (cf. K_1 for the dibutyltin dichloride/TPPO and tributyltin chloride/TPPO adducts of 122 and 6, respectively), (b) that the order of base strengths is TEPO > TPPO > DMA > acetonitrile, and (c) that butyltin trichloride is the weakest acid, whereas methyltin trichloride is the strongest acid toward acetonitrile, but phenyltin trichloride is the strongest acid toward TPPO and TEPO. The formation of the butyltin trichloride/TPPO adduct was studied by ^{119}Sn NMR in chlorobenzene and by ^{31}P in benzene. The constants obtained were in good agreement, 3×10^3 and 5×10^3, respectively. The constants obtained by ^{119}Sn NMR for the acetonitrile adduct in chlorobenzene are also in good agreement with those obtained by calorimetry in benzene.

The acidity order: $C_6H_5SnCl_3 > CH_3SnCl_3 > C_4H_9SnCl_3$, for the phosphine oxides can be explained with a combination of steric hindrance and inductive effect. Although the phenyl group is larger than methyl, it is electron-withdrawing and in previous studies has been shown to generally confer greater acidity on the tin site [6,7]. The methyl group is smaller than butyl (and probably slightly less electron-releasing) and usually results in the greatest acidity for alkyl cogeners [6.7]. For acetonitrile, a small linear base, steric effects might be expected to be less important. At present, the experimentally smaller K for the phenyl derivative cannot be explained.

The trend toward an increasing percentage of 1/2 adduct as both the acidity of the acid and the basicity of the base increase must be noted. In the present study this is apparent both from schematic mapping of calorimetric data and from the increasing curvature of the NMR plots as the strength of the base increases. The data of this study also demonstrate that the most acidic organotin acids, the organotin trihalides, indulge in greater formation of 1/2 adducts than their weaker cogeners, the mono- and di-halides. It must be emphasized, however, that for all of the organotin halide/base systems studied the 1/1 adduct is favored in solutions that are initially equimolar in acid and base.

Finally, previous studies have shown a pronounced solvent effect on the equilibrium parameters for these systems. Both benzene and chlorobenzene are strongly solvating for both acid and base. This solvation presumably arises principally from dispersion and dipolar interactions between the solvent and solute. Solvation probably increases in the order $CH_2Cl_2 >$ benzene $>$ chlorobenzene. Thus, equilibrium constants and enthalpies will be affected in the same order, i.e., K and ΔH will be smaller in the more solvating medium.

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 See for example V.S. Petrosyan, N.S. Yahina, and O.A. Reutov, Adv. Organomet. Chem., 14 (1976) 63 and G.P. Van Der Kelen, E.V. Van Den Berghe, and L. Verdonck, in A.K. Sawyer (Ed.), Organotin Compounds, Marcel Dekker, New York, New York, Vol. 1, 1971.

2 H. Fujiwara, F. Sakai, Y. Mikawa, and Y. Sasaki, Bull. Chem. Soc. Jpn, 58 (1985) 1741.

3 H. Fujiwara, F. Sakai, and Y. Sasaki, J. Chem. Soc., Perkin Trans. 2 II, (1983) 11.

4 H. Fujiwara, F. Sakai, and Y. Sasaki, J. Phys. Chem., 83 (1979) 2400.

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

6 J.N. Spencer, S.W. Barton, B.M. Cader, C.D. Corsico, L.E. Harrison, M.E. Mankuta, and C.H. Yoder, Organometallics, 3 (1985) 394.

7 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.

8 S.-W. Ng, C.L. Barnes, M.B. Hossain, D. van der Helm, J.J. Zuckerman, and V.G. Kumar Das, J. Am. Chem. Soc., 104 (1982) 5359; A.L. Rheingold, S.-W. Ng, and J.J. Zuckerman, Organometallics, 3 (1984) 233.

9 M.H. Abraham, P.P. Duce, R.A. Schulz, J.J. Morris, P.LJ. Taylor, and D.G. Barratt, J. Chem. Soc. Faraday Trans. I, 82 (1986) 3501.

10 J. Mullens, J.P. Yperman, and L.C. Pouke, J. Phys. Chem., 89, (1985) 2937.

11 J.N. Spencer, S.M. Coley, J.C. Otter, A. Grushow, B.G. Enders, W.L. Nachlis, and C.H. Yoder, J. Organomet. Chem., 346 (1988) 161.