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Phosphonate Ester Complexes of Methyltin Chlorides. Formation Constant as a Function of Nuclear Spin Coupling Constant

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The simultaneous evaluation of thermodynamic data along with the limit of the variable whose measurement provides the data has been successfully applied to systems involving non-isolable complexes in rapid equilibrium. A graphical method was first introduced to solve for ΔH and formation constant from calorimetric measurements [1], and an iterative curve-fitting technique has been used to find K and chemical shift of hydrogen bonded species from measurement of the observable chemical shift [2].

We have determined the formation constants and the directly bonded phosphorus–hydrogen nuclear spin coupling constants in some phosphonate ester complexes of methyltin chlorides by such a technique, and we present here the results of our preliminary investigation.

The very large increase in P–H coupling constants when phosphonate esters complex with Lewis acids [3] suggests their measurement as a sensitive parameter for the determination of equilibrium constants. In a rapid acid-base equilibrium $A + B \rightleftharpoons AB$ the relationship between coupling constant J and formation constant K is given by the linear relationship of eqn. 1,

$$\frac{1}{J_{obs} - J_B} = \frac{1}{KA(J_{AB} - J_B)} + \frac{1}{J_{AB} - J_B} \tag{1}$$

in which the observable coupling constant is related to mole fractions of the NMR active species as $J_{obs} = X_B J_B + X_{AB} J_{AB}$. The equilibrium concentration A can be related to initial concentrations A_0 and B_0 by eqn. 2.

$$A = \frac{1}{2}\left(A_0 - B_0 - \frac{1}{K} + \left[\left(B_0 - A_0 + \frac{1}{K}\right)^2 + \frac{4A_0}{K}\right]^{\frac{1}{2}}\right) \tag{2}$$

If observable quantities are plotted in accordance with eqn. 1 using approximate values of A, the value of K defined by the slope and intercept can be used in eqn. 2 to yield a better set of A values. Successive iterations will improve K and A, and thus also J_{AB}.

Coupling constant measurements were made on the esters $(CH_3O)_2PHO$, $(C_2H_5O)_2PHO$ and $(C_6H_5O)_2PHO$ in combination with the acids $(CH_3)_2SnCl_2$ and $(CH_3)_3SnCl$. Increments of acid were added to solutions of the esters in dichloromethane, and nmr spectra were recorded at 35 °C. Solution densities were determined after each addition of acid to allow calculation of K as liters/mole.

The magnitude of K in these systems proved to be too large to treat the data by this iterative process. The initial approximation $A = A_0$ was so far from valid that successive iterations were providing only infinitesimal corrections long before the correct values were approached. However, the more powerful simplex curve-fitting technique [4] proved satisfactory. To avoid the inherent imprecision in the $1/\Delta J$ terms, eqn. 1 was inverted and rearranged thus:

$$J_{obs} - J_B = \frac{KA(J_{AB} - J_B)}{1 + KA}. \tag{3}$$

The simplex program was provided with initial approximations to K and J_{AB} which were obtained from the unsuccessful iterative method. The simplex systematically varied these values to provide the best fit to all data pairs, J_{obs} and $A = f(A_0, K)$, as determined by minimization of the sum of the squares of differences in values of the two sides of eqn. 3. The computerized simplex routine was terminated when successive values of J_{AB} and K were invariant to the fifth significant figure.

The results are presented in the following table. The last digit in each entry arises from the averaging of results of repeated runs, and is not an indication of precision.

	$(CH_3O)_2PHO$ (J = 694 Hz)		$(C_2H_5O)_2PHO$ (J = 689 Hz)	
	J_{AB}	K	J_{AB}	K
$(CH_3)_2SnCl_2$	728.5	7.95	718.5	15.5
$(CH_3)_3SnCl$	725.0	0.38	717.5	0.52

Diphenyl phosphonate (J = 733 Hz) was investigated with $(CH_3)_3SnCl$ only, and was found to have $J_{AB} = 762$ and $K = 0.13$. Data were also collected for methyltin trichloride complexes, however they did not conform to the evaluation procedure described. This may be a consequence of additional equilibria involving a 2:1 complex or an ionic species with this stronger acid. Measurement of the ^{119}Sn–H coupling constant has been used for evaluation of other methyltin chloride complexes [5], but we did not observe sufficient variation in its magnitude for meaningful curve-fitting.

The best value of K from each simplex routine was used in eqn. 2 to generate a set of A values for substitution into eqn. 1. The latter gave a line whose slope and intercept yielded values K' and J'_{AB}, and the degree of agreement between these and the simplex values provided a sensitive check on the success of curve fitting. Values of K and K' agreed within 5% and J and J' were within one Hz, or the simplex curve-fitting was considered unsuccessful. Deranleau has shown that good curve-fitting requires measurements over a wide range of percent base complexed [6], and our range was somewhat limited by the magnitudes of the formation constants and the solubilities of the Lewis acids. We are consequently undertaking a variable temperature study to obviate these limitations as well as to secure additional thermodynamic data on the complexes.

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