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Study of halogen exchanges in (Z)-1-[2-(Bromochlorophenylstannyl)vinyl]-1-cyclohexanol by 2D ^{119}Sn EXSY NMR

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Abstract

The halogen exchange reactions at equilibrium of (Z)-1-[2-(bromochlorophenylstannyl)vinyl]-1-cyclohexanol were studied by two-dimensional ^{119}Sn exchange NMR spectroscopy (2D ^{119}Sn EXSY NMR). A single halogen exchange mechanism was found from a quantitative matrix analysis of the data.

Keywords: Tin; 2D EXSY NMR; Halogen exchange

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1. Introduction

We reported recently the synthesis and characterization of (Z)-1-[2-(triphenylstannyl)vinyl]-1-cyclohexanol and its phenylhalostannyl derivatives [1]. Among these, the bromochlorophenyl derivative, (Z)-1-[2-(bromochlorophenylstannyl)vinyl]-1-cyclohexanol (**2**) exhibited, in $CDCl_3$ solution, three ^{119}Sn resonances in the intensity ratio 1:2:1. On the basis of the expected relative shielding effects of Br and Cl, these resonances were tentatively assigned to $RPhSnCl_2$ (**1**), RPhSnBrCl (**2**), and $RPhSnBr_2$ (**3**), respectively, which are suggested to exist as an equilibrium mixture generated upon dissolution of pure **2**. Accordingly, halogen exchange reactions [2,3] were considered as slow on the ^{119}Sn NMR time scale [1]. Further indirect evidence for this exchange was provided by the fact that **2** exhibited single averaged resonances (or resonance patterns) for each atom type in the $\{^1H\}$-^{13}C spectra (or ^1H spectra) [1]; this suggested that the exchange is fast on the ^1H and ^{13}C NMR time scales.

Two-dimensional exchange NMR spectroscopy (2D EXSY) has been applied previously to the ^{119}Sn nucleus [2,4], but use of this powerful technique for kinetic studies of exchange between organotin species under equilibrium conditions is uncommon. We report below the results of the application of this technique to the study of the halogen exchange reactions at equilibrium in the mixture of $RPhSnCl_2$ (**1**), RPhSnBrCl (**2**) and $RPhSnBr_2$ (**3**) mentioned above.

2. Experimental section

The sample used for the 2D EXSY experiments was prepared by adding 18 mg of **1** and 12 mg of **3** to a solution containing initially 30 mg of **2** in 0.5 ml of $CDCl_3$.

All spectra were recorded at 30°C at 186.50 MHz on a Bruker AMX500 spectrometer interfaced with an X32 computer and equipped with a 5 mm selective $^{119}Sn\{^1H\}$ probe head. ^{119}Sn chemical shifts are given with respect to $Me_4{}^{119}Sn$ in $CDCl_3$ as external reference. The 1D $^{119}Sn\{^1H\}$ spectra were acquired in the inverse gated decoupling mode [5]. An interpulse delay of 2 s was chosen to ensure the relative ^{119}Sn reso-

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nance integrations to be representative of the species populations. Ten 2D $^{119}Sn\{^1H\}$ EXSY spectra were recorded in the phase-sensitive mode (TPPI[6]) using the pulse sequence of Jeener et al. [7] with mixing times of 5, 6, 7, 8, 9, 10, 12, 14, 16 and 18 ms. An additional experiment was performed with a mixing time of 0 ms. The recycling delay was 2 s. 96 $(t_1) \times 1024(t_2)$ data points were recorded with 128 scans and zero-filled to 512 $(t_1) \times 1024(t_2)$ for a spectral width of 17857 Hz.

An exponential window function with 120 Hz line-broadening was applied in both dimensions prior to double Fourier transformation. The auto- and cross-peak volumes were determined by use of the standard Bruker UXNMR software after phase and baseline corrections in both dimensions. The matrix calculations were performed on an Apple Macintosh II computer using the Edu-MATLAB 1.0 software [8].

3. Results and discussion

The standard 1D $^{119}Sn\{^1H\}$ NMR spectrum of a pure sample (30 mg) of RPhSnBrCl (**2**) in $CDCl_3$ revealed the pattern observed previously [1], consisting of three resonances at −132.1, −158.5 and −185.9 ppm with relative integrals of 0.25, 0.50 and 0.25 (within experimental error). After addition of $RPhSnCl_2$ (**1**) (18 mg), and $RPhSnBr_2$ (**3**) (12 mg), the three resonances with the same chemical shifts were present but the relative integral areas were 0.33, 0.48 and 0.19, respectively. These are identical, within experimental error, to the statistical distribution expected from the above composition of **1**, **2** and **3**. Accordingly, these results unambiguously identify the three resonances at −132.1, −158.5 and −185.9 ppm as coming from $RPhSnCl_2$ (**1**), RPhSnBrCl (**2**) and $RPhSnBr_2$ (**3**), respectively, as expected from the higher shielding effect of bromine than of chlorine. The subsequent 2D EXSY experiments were performed on the latter equilibrium mixture.

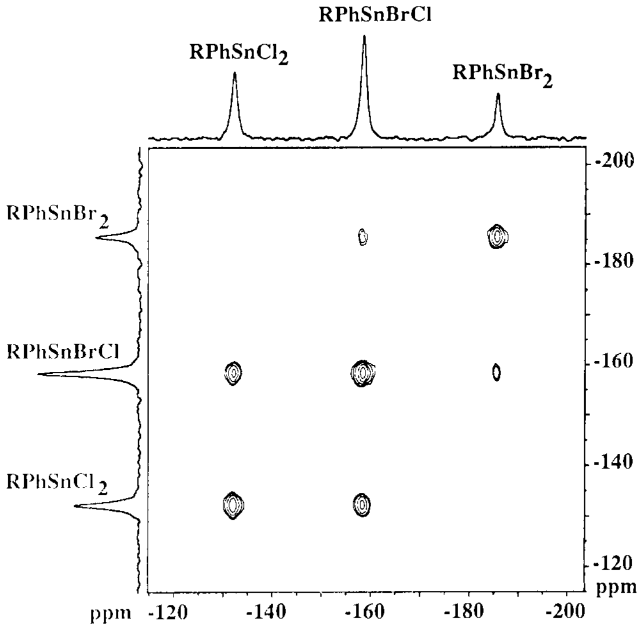

Fig. 1. Contour plot of the 2D $^{119}Sn\{^1H\}$ EXSY spectrum recorded for a mixing time of 18 ms. The corresponding 1D $^{119}Sn\{^1H\}$ spectra are plotted along the axes.

Fig. 1 shows a contour plot of the results obtained with an 18 ms mixing time as an example of the 2D phase-sensitive $^{119}Sn\{^1H\}$ EXSY spectra obtained. Ten such EXSY spectra were recorded with mixing times (t_m) ranging from 5 to 18 ms. For shorter mixing times no cross-peaks were observed (0.9 and 1 ms) or the bad signal-to-noise ratio prevented reliable analysis (2, 3 and 4 ms). The cross-peak volumes were identical within experimental error (typically 10%) for pairs symmetrical with respect to the diagonal [9]. The data were analyzed using two variants of the normal mode analysis of Perrin and Gipe [9–11]. The first one is based on method B described in Ref. 11, using the measured normalized cross-peak volumes $\mathbf{A}_{ij}(t_m) = \mathbf{V}_{ij}(t_m)/\mathbf{V}_{jj}(t_m = 0)$ of the EXSY map. The second variant, based on method C described in Ref. [11] symmetrizes the cross-peak volume matrix, in order to smooth out experimental errors, $\tilde{\mathbf{V}}_{ij}(t_m) = [\mathbf{V}_{ij}(t_m) + \mathbf{V}_{ji}(t_m)]/2$, prior to normalization to the diagonal peak volumes of the zero mixing time experiment, $\mathbf{A}_{ij}(t_m) = \tilde{\mathbf{V}}_{ij}(t_m)/\tilde{\mathbf{V}}_{jj}(t_m = 0)$.

The exchange matrix **L**, shown below, can then be calculated from the relationship [9–11],

$$\mathbf{L} = (1/t_m)\ \ln \mathbf{A} = (1/t_m)\mathbf{U}(\ln \boldsymbol{\lambda})\mathbf{U}^{-1}$$

where **U** and λ are the matrices of the eigenvectors and eigenvalues respectively, of **A** and ln λ is the diagonal matrix of the ln λ_j elements.

$$\mathbf{L} = \begin{bmatrix} -R_1^1-(k_1+k_3) & k_{-1} & k_{-3} \\ k_1 & -R_1^2-(k_{-1}+k_2) & k_{-2} \\ k_3 & k_2 & -R_1^3-(k_{-2}+k_{-3}) \end{bmatrix}$$

with

$$RPhSnCl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RPhSnBrCl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RPhSnBr_2$$

and

$$RPhSnCl_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RPhSnBr_2$$

In the above schemes, the constants k_j and k_{-j} are the pseudo-first-order constants directly measurable, in s^{-1}, from the cross-peak volumes in the 2D EXSY spectrum [9]. They involve kinetic parameters characteristic for the second species involved in the halide exchange as a source of the necessary halide moieties [2,3,9], e.g.: $k_1 = k_{12}[2] + k_{13}[3]$. R_1^i represents the longitudinal relaxation rate of the ^{119}Sn resonance of species **i** (**1** = $RPhSnCl_2$; **2** = RPhSnBrCl; **3** = $RPhSnBr_2$). The final results, expressed as mean rate constants in s^{-1} (from ten experiments ± SD) obtained by the two methods, are shown below:

$$\mathbf{L}' = \begin{bmatrix} -37.0 \pm 5.1 & 25.1 \pm 3.8 & -1.4 \pm 4.0 \\ 33.4 \pm 7.7 & -30.1 \pm 3.1 & 16.0 \pm 4.5 \\ 0.4 \pm 2.4 & 5.7 \pm 1.7 & -22.7 \pm 6.2 \end{bmatrix}$$

method B

$$\mathbf{L}'' = \begin{bmatrix} -37.1 \pm 5.1 & 23.8 \pm 4.1 & -0.3 \pm 3.0 \\ 35.3 \pm 6.1 & -30.2 \pm 3.1 & 15.4 \pm 3.9 \\ -0.2 \pm 1.7 & 5.9 \pm 1.5 & -22.7 \pm 6.1 \end{bmatrix}$$

method C

There is no statistically significant difference between the elements of $\mathbf{L}'$ and $\mathbf{L}''$. The elements connecting species **1** and **3** are not significantly different from zero. The other nondiagonal elements display variation coefficients of ca. 20%. This relatively high value reflects the poor signal to noise ratio due to the high natural line width (40 Hz) and to the relatively low concentration. Nevertheless, the conclusion that the exchange occurs through single halogen exchange is unambiguous.

The equilibrium exchange rate between $RPhSnCl_2$ and RPhSnBrCl is about four times larger than between RPhSnBrCl and $RPhSnBr_2$; this suggests an increasing effect of steric hindrance of bromine upon halogen exchange.

The weak cross-peaks associated with the double halogen exchange $RPhSnCl_2 \rightleftharpoons RPhSnBr_2$, observed at longer mixing times, can unambiguously be assigned to a relayed two step process; this is supported by the associated rate constants in the matrices $\mathbf{L}'$ and $\mathbf{L}''$, which are not statistically different from zero, as pointed out above.

The 2D EXSY experiments enable a rough estimation of the longitudinal relaxation times $T_1^j = 1/R_1^j$. The R_1^j values were evaluated by subtracting the diagonal element $\mathbf{L}''_{jj}$ of the matrix $\mathbf{L}''$ from the sum of the significant non-zero non-diagonal elements of the column j of $\mathbf{L}''$. The longitudinal relaxation times thus obtained are: $T_1^1 = 0.6 \pm 0.2$ s and $T_1^3 = 0.14 \pm 0.07$ s while no statistically significant value was obtained for T_1^2. This, as well as the high standard deviations of the other T_1^j values, results from the fact that the corresponding R_1^j are small values obtained from differences between two large numbers, the exchange rates being much larger than the longitudinal relaxation rates. These values should therefore be considered with extreme care.

In conclusion, as for allyltin trihalides [3] and tin tetrahalides [2], only a single halogen is exchanged at one time in the present compounds, probably by a bimolecular mechanism involving hexacoordinated tin atoms in an intermediate complex. We suggest that the intramolecular HO → Sn interaction labilizes the tin–halogen bonds in such an intermediate, and hence promotes the halogen exchange.

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References

[1] F.F. Xin, S.X. Lin, F.Y. Jie, H. Pan, B. Mahieu, M. Gielen, F. Kayser and R. Willem, *Z. Anorg. Allg. Chem.*, in press.

[2] R. Ramachandran, C.T.G. Knight, R.J. Kirkpatrick and E. Oldfield, *J. Magn. Reson.*, *65* (1985) 136.

[3] I. Pianet, E. Fouquet, M. Pereyre, M. Gielen, F. Kayser, M. Biesemans and R. Willem, *Study of Halogen Exchange in Allyltin Trihalides by Two-dimensional* ^{119}*Sn EXSY NMR*, submitted.

[4] (a) C. Wynants, G. Van Binst, C. Mügge, K. Jurkschat, A. Tzschach, H. Pepermans, M. Gielen and R. Willem, *Organometallics*, *4* (1985) 1906; (b) V.K. Jain, V.B. Mokal and P. Sandor, *Magn. Reson. Chem.*, *30* (1992) 1158; (c) X. Mao, X. You and A. Dai, *Bopuxue Zazhi 7* (1990) 61 (*Chem. Abstr. 113*, 66227n); (d) X. Mao, X. You and A. Dai, *Magn. Reson. Chem.*, *27* (1989) 836.

[5] R. Freeman, H.D.W. Hill and R. Kaptein, *J. Magn. Reson.*, *7* (1972) 327.

[6] (a) D. Marion and K. Wüthrich, *Biochim. Biophys. Res. Commun.*, *113* (1983) 967; (b) G. Bodenhausen, H. Kogler and R.R. Ernst, *J. Magn. Reson.*, *58* (1984) 370.

[7] J. Jeener, B.H. Meier, P. Bachmann and R.R. Ernst, *J. Chem. Phys.*, *71* (1979) 4546.

[8] C. Moler, S. Herskovitz, J. Little and S. Bangert, Edu-MATLAB, Vers. 1.0 (1988).

[9] R. Willem, *Prog. NMR Spectrosc.*, *20* (1987) 1.

[10] (a) C.L. Perrin and R.K. Gipe, *J. Am. Chem. Soc.*, *106* (1984) 4036; (b) C.L. Petrin and T.J. Dwyer, *Chem. Rev.*, *90* (1990) 935.

[11] R. Willem, M. Biesemans, K. Hallenga, G. Lippens, F. Malaisse-Lagae and W.J. Malaisse, *J. Biol. Chem.*, *267* (1992) 210.