Halogen exchange in substituted allyltin halides studied by 2D NMR EXSY as a tool to assess reactivity

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Abstract

The halogen exchange between two monoallyltin compounds has been investigated by ^{119}Sn 2D NMR EXSY. It is demonstrated that the slower halogen exchange observed in the allylbisN,N(bistrimethylsilyl)aminotin halide compared with the allyltin trihalides can be correlated with the dramatic change in reactivity of these compounds in allyl radical transfer.

1. Introduction

In a previous paper [1], we outlined the power of 2D ^{119}Sn EXSY NMR as a tool for the investigation of halogen scrambling reactions in allyltin trihalides RSnX$_3$ (R = crotyl, allyl; X = Cl, Br). We demonstrated that this scrambling involves a single halogen exchange through an intermediate with two trihalide moieties. The present paper describes both the study of bromine–iodine exchange between two novel monoallyltin compounds by a similar NMR methodology and the reactivity of the compounds. Compounds 1 and 2 were prepared by the reaction of Lappert's stannylene [2] with the appropriate allyl halide (Scheme 1). [Compound 1: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.16 (qt, J 7.1, 1.7, 1H), 4.41 (q, J 7.1, 2H), 2.37 (dq, J 1.7, 1.5, 2H, degenerated to a pseudo-quintet with apparent $J \approx 1.6$), 2.00 (dt, J 7.1, 1.5, 3H), 1.34 (t, J 7.1, 3H), 0.22 (s, 36H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 172.5, 141.0, 128.4, 63.3, 30.4, 15.7, 14.1, 6.2. Compound 2: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.17 (qt, J 7.1, 1.7, 1H), 4.41 (q, J 7.1, 2H), 2.76 (dq, J 1.7, 1.5, 2H, degenerated to a pseudo-quintet with apparent $J \approx 1.6$), 2.05 (dt, J 7.1, 1.5, 3H), 1.45 (t, J 7.1, 3H), 0.22 (s, 36H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 170.5, 139.4, 128.3, 62.3, 32.4, 16.0, 14.0, 6.4.]

This system presents the advantage of having only one site of halogen exchange instead of three, as a consequence of the substitution of two halogens for two bis(trimethylsilyl)amino moieties. The bis(trimethylsilyl)amino groups do not exchange on the ^{119}Sn NMR timescale because the silicon atoms impart a special strength to the tin–nitrogen bonds compared with more conventional amino groups.

Under such conditions, it is possible to keep the concentration of the functional allylbisN,N(bistrimethylsilyl)aminotin halides under control when halogen scrambling occurs between two such compounds differing only in the nature of the halogen. The present paper describes the dependence of the pseudo-first-order rate constants for the halogen exchange between the bromide 1 and iodide 2 on their concentration. The rate constant values are assessed in the light of both the exchange mechanism and the reactivity of the functionalized allyltin compound.

2. Experimental

2.1. Sample preparation

Four samples were prepared using different concentrations of 1 and 2 in CDCl$_3$ (see Table 1). The samples were deoxygenated for 5 min in an ultrasonic bath under

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Scheme 1.

Scheme 2.
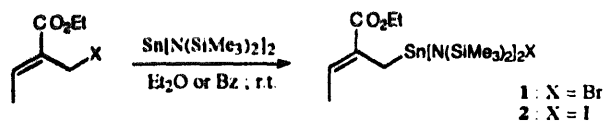
argon atmosphere, so as to keep T1 relaxation under control and to minimize cross-peak intensity loss upon mixing time increase.

2.2. ^{119}Sn NMR spectroscopy

1D and 2D ^{119}Sn spectra of all four samples were recorded on a Bruker DPX 400 equipped with an Aspect station one computer and a 5 mm inverse broad band probe tuned at 149.2 MHz for ^{119}Sn nuclei.

The 1D ^{119}Sn{^{1}H} spectra from all four samples were acquired in the inverse gated decoupling mode [3], using a spectral width of 15 kHz, 16 K memory size, 2.04 s interpulse delay and 32 scans. ^{119}Sn chemical shifts are given with respect to Me$_4$Sn in CDCl$_3$ as an external reference $\Xi(^{119}Sn) = 37.290665$ [4].

The 2D ^{119}Sn{^{1}H} NMR EXSY spectra were recorded in the phase sensitive mode with time proportional phase incrementation [5] using the basic pulse sequence of Jeener et al. [6] with proton decoupling only during the pulse sequence and signal acquisition. A standard 16-dimensional phase cycle, as set up in the Bruker microprogram library, was used. The total recycling delay was 2 s. The 90° pulse length (15.5 μs) was checked prior to each EXSY spectrum acquisition. The data point matrix was 256 (t_1) × 512 (t_2), the spectral width 15 kHz. The total experiment time was 4 h for all 2D spectra, which were recorded with 32 scans. The mixing times were 0, 50, 100, 150, 200, 300, 500 ms for sample 1; 0, 200, 300, 400, 500, 600, 800 ms for sample 2; 0, 20, 30, 40, 50, 60, 80, 100, 120, 150, 200, 300 ms for sample 3; and 0, 20, 30, 40, 50, 60, 80, 100, 120, 150 ms for sample 4. The mixing time was set at 3 μs for zero mixing time experiments. The auto- and cross-peak volumes were determined after phase and baseline corrections in both frequency dimensions using the Bruker UXNMR software.

2.3. Rate constants

The pseudo-first-order rate constants k_{ab} and k_{ba} (Scheme 2), as defined above, were determined by two different methods: the initial rate method [7] and the matrix method of Perrin and Gipe [8], in exactly the same way as explained elsewhere [1].

3. Results and discussion

The 1D ^{119}Sn NMR spectrum of a solution of pure 1 or 2 displays a single ^{119}Sn resonance at −167 or −236 ppm respectively. The ratios of integrated areas of auto-peak volumes of the resonances of 1 and 2 in their mixtures in samples 1 to 4 were found to be pairwise identical, within experimental error, to the concentration ratios used in the mixtures of 1 and 2, outlining conditions of full T1 relaxation during the total recycling delay of 2 s. Fig. 1 shows an example of build-up curves, as obtained from sample 4. The pseudo-first-order rate constants k_{ab} and k_{ba} are determined from their slopes. The numerical values for k_{ab} and k_{ba} are obtained both by the latter method [7] (method 1) and by the matrix method of Gipe and Perrin [8] (method 2) and are reviewed in Table 2. The agreement between the values of k_{ab} and k_{ba}, as obtained from the two methods, is generally good.
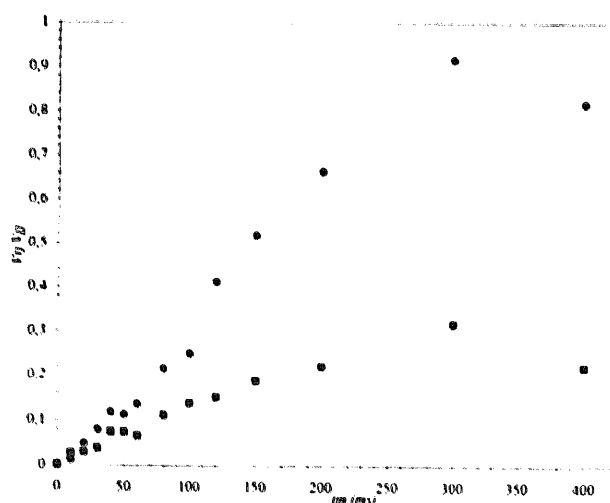
Table 1
Composition and NMR acquisition temperature of the four samples

Temperature (°C)	Sample	[X] (M) [a]	[Y] (M) [a]	Final volume (ml)
40	1	0.85	0.28	0.6
40	2	0.62	0.49	0.8
50	3	0.46	0.26	0.6
50	4	0.94	0.37	0.8

[a] X = RSn[N(SiMe$_3$)$_2$]$_2$Br; Y = RSn[N(SiMe$_3$)$_2$]$_2$I.

Fig. 1. Build-up curves displayed as $B_{ij} = V_{ij}/V_{jj}$ against the mixing time t_m illustrating the two halogen exchange of sample 4 from RSn[N(SiMe$_3$)$_2$]$_2$I to RSn[N(SiMe$_3$)$_2$]$_2$Br (●) and from RSn[N(SiMe$_3$)$_2$]$_2$Br to RSn[N(SiMe$_3$)$_2$]$_2$I (■).

Table 2
Measurement of the pseudo-first-order rate constant using the method of initial rate

Temperature (°C)	Sample	Method 1 *		Method 2 *	
		k_{ab}	k_{ba}	k_{ab}	k_{ba}
40	1	0.42 ± 0.04	1.51 ± 0.09	0.52 ± 0.06	1.43 ± 0.06
40	2	0.41 ± 0.02	0.76 ± 0.04	0.43 ± 0.04	0.72 ± 0.06
50	3	1.11 ± 0.06	3.36 ± 0.14	1.6 ± 0.3	2.7 ± 0.4
50	4	2.2 ± 0.2	7.0 ± 0.8	2.3 ± 0.4	6.9 ± 1.3

* Values expressed in s^{-1} ± SE for method 1 and ± SD for method 2.

As observed previously for the $RSnCl_2Br$ compound [1], the rate constants k_{ab} and k_{ba} display a concentration dependence which reflects a bimolecular process (Scheme 3). They can be expressed as:

$$k_{ab} = k_1[SnI] \quad \text{and} \quad k_{ba} = k_{-1}[SnBr]$$

where SnI and SnBr stand for $RSn[N(SiMe_3)_2]_2I$ and $RSn[N(SiMe_3)_2]_2Br$ respectively. Given that the equilibrium concentrations are well defined in the present two-site exchange case, the values of k_1 and k_{-1} should be identical according to the mass action law if the reaction mechanism proposed above is the actual one. The values of k_1 and k_{-1} obtained by the equation above and presented in Table 3 demonstrate this to be the case within experimental error, even if a rather large dispersion, assigned to signal-to-noise ratio, is noted. An intermediate in the possible mechanism for this bimolecular exchange is proposed in Scheme 4.

The access to quantitative exchange data of this type is of paramount importance for synthetic purposes, as the halogen present in hypervalent organometallic intermediates often appears to modulate strongly the reactivity of the carbon–metal bond of the functionalized organic group bound to tin [9]. Thus, the difference in halogen exchange rates observed with compounds 1 and 2, compared with the allylSnX₃ ones, is to be correlated with the dramatic change in reactivity exhibited by these allylic tin reagents in allyl radical transfer reactions (Scheme 5) [10].

The generation of the two products in these reactions results from competition between two possible halogen
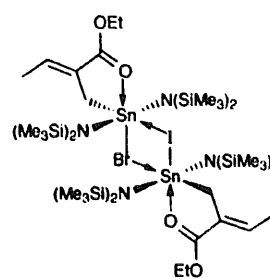

Scheme 4.

abstractions by the tin centered radicals, $^•SnCl_2Br$ and $^•Sn[N(SiMe_3)_2]_2Br$ respectively (Scheme 6).

Theoretical calculations performed with two semi-empirical methods (MNDO [11], AM1 [12]) aimed at finding the relative energies of the tin centered radical single occupied molecular orbitals indicate a dramatic increase in nucleophilicity of the radicals upon substitution of the halogen moieties for bis(trimethylsilyl)amino ones. Considering the higher electron density of a bromine bound to a tin atom compared with a bromine bound to a carbon one, the rate of bromine abstraction on the allylic tin reagent (pathway 2) versus the abstraction on the alkyl halide (pathway 1) is expected to be slowed down when bis(trimethylsilyl)amino ligands rather than halogens are present. The regioselectivity inversion in the reactions is then readily accounted for. These experimental reactivity findings are fully consistent with our 2D EXSY NMR studies indicating dramatically lower exchange rates in the allylSn[N(SiMe₃)₂]₂X compounds compared with allylSnX₃ ones. This is even more remarkable in view of the fact that bromine–iodine exchange is considered in the former, while the expected intrinsically slower chlorine–bromine exchange was investigated in the latter [1].

Y = N(SiMe₃)₂

Scheme 3.

Table 3
Determination of the rate constants of the exchange between I and Br

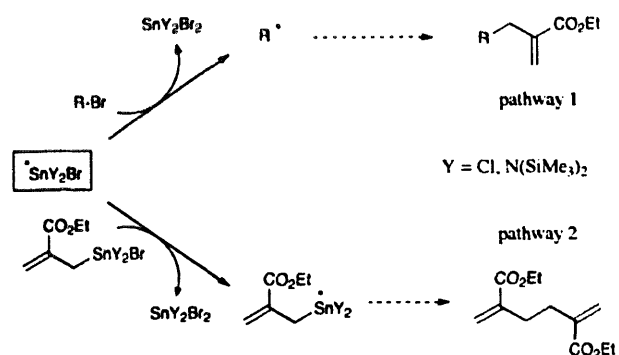| Temperature (°C)	k_1 *	k_{-1} *
40	1.3 ± 0.5	1.5 ± 0.3
50	5.7 ± 0.9	6.9 ± 0.8

* Values expressed in $M^{-1}s^{-1}$.

Scheme 5.

SnY₂Br₂

R·

R‑Br

RCO₂Et

pathway 1

SnY₂Br

Y = Cl, N(SiMe₃)₂

CO₂Et
SnY₂Br

pathway 2

SnY₂Br₂

CO₂Et
SnY₂

CO₂Et
CO₂Et
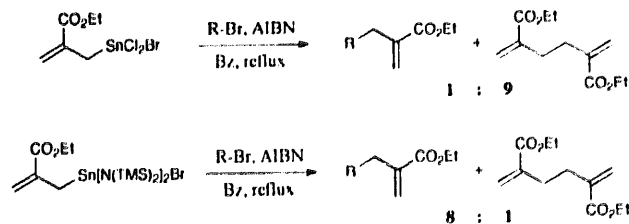
Scheme 6.

In conclusion, the results of the present investigation highlight how the chemical reactivity of allylic organotin compounds is correlated with the exchange rates of moieties displaying labile bonds with the tin center.

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