A Two-Dimensional NMR Approach to the Study of Intermolecular Scrambling Reactions

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Redistribution or scrambling reactions (1) are of considerable importance and are commonplace in the chemistry of silicon, germanium, tin, and lead (2). Redistribution reactions occurring in mixtures of tin(IV) tetrahalides have long been the subject of research (3) and it is well established (4) that these mixtures equilibrate rapidly at room temperature to yield a statistical distribution of all possible mixed halide species. Despite being the subject of the first reported ¹¹⁹Sn NMR study (4), the kinetics and mechanism of these processes have received little attention. This is perhaps not surprising given the existence of several simultaneous exchange pathways.

We thus report in this Note the results of a two-dimensional chemical-exchange (5) ¹¹⁹Sn NMR spectroscopic study of the kinetics of the halide redistribution reactions occurring in a 1:1 *M* mixture of SnCl₄ and SnBr₄, at 340 K. We believe this to be the first example of the application of two-dimensional NMR (6) to the tin-119 nucleus, and the first example of an intermolecular scrambling reaction to be investigated using 2D methods. The unidirectional, pseudo-first-order rate constants of the four exchange processes governing the solution dynamics in this system are reported. The exchange rates are found to be dependent upon the nature of the exchanging sites, and our results also strongly suggest that only single halide exchanges occur.

Tin-119 NMR spectra were recorded at 186.4 MHz using a "home-built" 11.7 T NMR spectrometer. A Nicolet 1280 data system equipped with a Nicolet 293 B pulse programmer was employed, using a "home-built" interface (7) between the pulse programmer and spectrometer to achieve computer-controlled phase cycling of the transmitter rf pulses. A 16-step phase cycling for *N*-type peak selection (8) was implemented with quadrature detection in both dimensions, over a spectral width of 125 kHz. The 90° pulses used were 5 μ s in length, and τ_m values ranging from 1 to 250 ms were employed. A 256 × 1 K two-dimensional data matrix was generated using the pulse sequence 90°- t_1 -90°- τ_m -90°- t_2 -(acquisition), with a total of 192 scans per t_1 value (incremented by 8 μ s). Zero filling in the t_1 domain was used to improve spectral appearance.

The sample was prepared in an inert atmosphere, using high-purity commercially available reagents, particular attention being paid to the exclusion of atmospheric moisture. The sample was static, being sealed in a section of 10 mm NMR tube and mounted in a solenoidal rf coil. All chemical-shift values are referenced to external $Sn(CH_3)_4$, signals resonating to high frequency of this being denoted as positive. The ¹¹⁹Sn chemical shifts of $SnCl_4$, $SnCl_3Br$, $SnCl_2Br_2$, $SnClBr_3$, and $SnBr_4$ are -151.6, -267.7, -388.7, -513.3, and -640.3 ppm, respectively, and are consistent with previously reported values (4, 9).

We show in Fig. 1 spectra obtained at four representative mix-time values. As the mix time is increased, halide scrambling causes magnetization transfer between the various spin-labeled sites, giving rise successively to all possible first-order (Fig. 1B), second-order (Fig. 1C), and third-order (Fig. 1D) cross peaks (fourth-order cross peaks are clearly visible in spectral cross sections of Fig. 1D although they are not apparent in the stacked plot). The appearance of second- (and higher) order cross peaks indicates magnetization transfer between species differing by two or more halogens. In principle, this may arise either by a series of relayed, single halide exchange steps, or by a one-step, multiple halide exchange, in which two or more halogens are swapped during



FIG. 1. Tin-119 2D absolute-value-mode NMR spectra of a 1:1 M mixture of SnCl₄ and SnBr₄ at 340 K and 186.4 MHz, as a function of the mix time, τ_m . The pulse sequence described in the text was used, with 192 scans per t_1 value, incremented by 8 μ s, with a recycle time of 0.5 s. An exponential line-broadening function of 100 Hz was applied in both dimensions. Chemical shifts are in parts per million from an external standard of tetramethyltin.

the lifetime of the transition state. However, second- and third-order cross peaks appear only after an induction period, typically of ~ 20 and ~ 40 ms, respectively, as shown in Fig. 2. Such behavior strongly suggests (8, 10, 11) a relayed transfer of magnetization, which implies that the scrambling proceeds via a series of single halide exchange steps.

On the assumption that the single halide exchange process takes place via bimolecular collisions, each first-order cross peak can then arise via several exchange pathways. For example, there are four possible pathways capable of transferring magnetization from $SnCl_4$ to $SnCl_3Br$:

$$\operatorname{SnCl}_4 + \operatorname{SnCl}_3 \operatorname{Br} \frac{k_1}{k_{-1}} \operatorname{SnCl}_3 \operatorname{Br} + \operatorname{SnCl}_4$$
[1]

$$\operatorname{SnCl}_4 + \operatorname{SnCl}_2\operatorname{Br}_2 \xrightarrow{k_2} \operatorname{SnCl}_3\operatorname{Br} + \operatorname{SnCl}_3\operatorname{Br}$$
 [2]

$$SnCl_4 + SnClBr_3 \stackrel{k_3}{\underset{k_{-3}}{\leftarrow}} SnCl_3Br + SnCl_2Br_2$$
[3]

$$\operatorname{SnCl}_4 + \operatorname{SnBr}_4 \frac{k_4}{k_{-4}} \operatorname{SnCl}_3 \operatorname{Br} + \operatorname{SnClBr}_3.$$
 [4]

In terms of the individual bimolecular rate constants, k_i , the unidirectional pseudofirst-order rate constant $K_{\text{SnCl}_4 \rightarrow \text{SnCl}_3\text{Br}}$ can be expressed as

$$K_{\text{SnCl}_4 \to \text{SnCl}_3\text{Br}} = k_1[\text{SnCl}_3\text{Br}] + k_2[\text{SnCl}_2\text{Br}_2] + k_3[\text{SnClBr}_3] + k_4[\text{SnBr}_4].$$
[5]

The relationship between the 2D first-order cross-peak intensities and exchange rate constants is given by (12, 13)

$$I_{ij} = (e^{-R\tau_{\rm m}})_{ij}M_j^0$$
 [6]

where M_j^0 is the equilibrium magnetization of the nuclei in site *j*, and *R* is the rate matrix having the off-diagonal elements $R_{ij} = -k_{ji}$, where k_{ji} is the first-order rate



FIG. 2. The time evolution of first- (\bigcirc), second- (\bullet) and third- (\triangle) order cross-peak volumes for the exchange processes between SnClBr₃ and SnCl₂Br₂, SnCl₃Br, and SnCl₄, respectively. 2D spectra were generated in the phase-sensitive mode and the relevant cross sections were manually phased to pure absorption. Peak volumes were obtained by integrating peak areas with respect to ω_2 , and summing those areas over ω_1 .

constant for chemical exchange from site j to site i. As τ_m tends to zero, Eq. [6] approaches the limiting form

$$I_{ij} = -R_{ij}\tau_{\rm m}M_j^0.$$
[7]

The diagonal peak volumes evaluated from the 2D spectrum obtained with $\tau_m = 1$ ms have been taken as representing the equilibrium magnetization, M_j^0 , of each species. The intensity ratios SnCl₄:SnCl₃Br:SnCl₂Br₂:SnClBr₃:SnBr₄ are 1.17:5.80:9.17:5.72: 1.00 (arbitrary units), excitation bandwidth limitations being primarily responsible for the deviations from the ideal (1:4:6:4:1) statistical distribution expected.

We show in Fig. 3 the cross-peak volume dependence on τ_m for the four different halide exchange processes possible in these solutions. From the initial slope, the unidirectional pseudo-first-order rate constants and, in turn, the appropriate exchange rates, may be derived, and are given in Table 1. The data satisfy, within experimental error, the requirement that forward and reverse rates be equal. Although, in principle, the individual bimolecular rate constants can be obtained from a study of the pseudofirst-order rate constants in solutions containing different equilibrium concentrations of the various species (Eq. [5]), such a study will be quite time-consuming and has not been attempted here.

The results we have presented above clearly reveal differential exchange characteristics in this system. For example, the rate of halide exchange from $SnCl_4$ to $SnCl_3Br$ is significantly greater than that of $SnBr_4$ to $SnClBr_3$. Similarly, the rate of exchange from $SnCl_3Br$ to $SnCl_2Br_2$ is greater than that of $SnClBr_3$ to $SnCl_2Br_2$. Although hitherto unobserved, such differences are consistent with the widely held view (14) that halide exchange proceeds via a four-centered transition state, formed as a result of a bimolecular collision, in which the halogens are simply "swapped" as indicated:

$$\operatorname{SnCl}_4 + \operatorname{SnBr}_4 \rightleftharpoons \operatorname{Cl}_3 \operatorname{Sn}_{\operatorname{Br}}^{\operatorname{Cl}} \operatorname{SnBr}_3 \rightleftharpoons \operatorname{SnCl}_3 \operatorname{Br} + \operatorname{SnClBr}_3.$$
 [8]



FIG. 3. The mix time dependence of the normalized first-order cross-peak volume for the following exchange processes: $SnCl_4 \rightarrow SnCl_3Br$ (\bigcirc), $SnCl_3Br \rightarrow SnCl_2Br_2$ (\bullet), $SnCl_2Br_2 \rightarrow SnClBr_3$ (\triangle), and $SnClBr_3 \rightarrow SnBr_4$ (+). The cross-peak volumes, obtained as in Fig. 2, were normalized to the respective diagonal-peak volumes obtained from the spectrum recorded with a mix time of 1 ms.

TABLE 1

Species		Pseudo-first- order rate constants $(s^{-1})^a$		Exchange rates (mol dm ³ s ⁻¹) ^b	
Α	В	K _{A→B}	K _{B→A}	$K_{A \to B}[A]$	$K_{\mathbf{B}\to\mathbf{A}}[\mathbf{B}]$
SnCl₄	SnCl ₃ Br	39	10	16	20
SnCl ₃ Br	SnCl ₂ Br ₂	12	9.0	25	29
SnCl ₂ Br ₂	SnClBr ₃	4.0	6.0	13	12
SnClBr ₃	SnBr₄	1.0	6.0	2.0	2.1

The Unidirectional Pseudo-First-Order Rate Constants and the Exchange Rates for Halide Exchange in a 1:1 *M* Mixture of SnCl₄ and SnBr₄ at 340 K

^{*a*} Errors are $\pm 15-25\%$.

^b The exchange rates are calculated from the concentrations of the species apparent in the 2D spectrum recorded with $\tau_m = 1$ ms.

Indeed, intermediates of this type have been suggested for most redistribution reactions (2, 14). The observed differences in the rates of the exchange processes may thus be rationalized in terms of steric effects alone, the bulkier bromine substituents hindering transition state formation. Thus, the use of 2D chemical-exchange NMR spectroscopy of the central atom involved should provide the opportunity to study many such exchange reactions, and under favorable circumstances, is capable of providing strong evidence as to exchange pathways, and an accurate method for determining exchange rates, both prerequisites in assigning reaction mechanisms.

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