$$K_2 = K_2'([Y_2]/[XY]) = k_{-1}[XY] + 2k_3[Y_2] \quad (19)$$

$$K_3 = K_3' = 0 \quad (20)$$

In this case all the pseudo-first-order rate constants can be individually determined, condition 11 being of course satisfied. The specific rate constants k_1, k_{-1}, k_2, and k_3 can in turn be solved for by varying the relative concentrations of the reactants.

Spin-Multiplet Structures

Questions always arise in chemical exchange problems involving spin coupled systems whether each component of a spin multiplet can be considered as an independent site. Usually when spin coupling is modulated by exchange without being interrupted by breaking of bonds between scalar coupled spins, the multiplet structures can always be considered as independent sites and if such bonds are broken whether spin multiplets can be considered as independent sites depends on whether there is spin coherence during the exchange or not. If spin orientation is conserved, multiplets then behave as independent sites. In fact if the multiplet independent site situation is established, the number of pseudo-first-order rate constants can be considerably reduced by the uniformity of the multiplet structure.

Discussion and Conclusion

The nuclear magnetic resonance (nmr) spectrum of a reacting mixture of compounds contains much more information of a quantitative analytical nature than the more classical methods of studying chemical kinetics. The measurement and analysis, for example, of a gas pressure or the record of the intensity of an ultraviolet absorption with time are very selective pieces of information and tell us very little about the reaction except the rate of growth or decay of one individual component with time. It is well known that nmr methods measure reaction rates at equilibrium and can also be used to follow the progress of reactions in nonequilibrium situations. The limitation of the method is the time window of the inverse frequency differences which are modulated by the exchange in the case where reactions are taking place at equilibrium. We have shown in this paper, the total information that can be derived from a complete line-shape fit approach to first-order spectra,[30] before an appeal to the chemical situation must be invoked to solve a reaction mechanism. An example of the application to a specific reaction is given in the following article.

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[30] Second order effects present no additional complication to this general analytical method though a spectrum with such effects will be more complex.

Mechanistic Studies of Chemical Exchange Reactions by Complete Nuclear Magnetic Resonance Line-Shape Fitting. II. 15-Site Halogen Exchange in Binary Mixtures of Dimethyltin Dihalides

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Abstract: The unsymmetric halogen exchange reactions of mixed dimethyltin dihalides in toluene solutions have velocities suitable for study by complete line-shape fit methods of exchange-broadened proton magnetic resonance spectra. The problem of modulation of 15 Larmor frequencies can be reduced to five equivalent sets of three, with no exchange between these five groups. In the 3 × 3 site rate matrix, tolerable line-shape fits can be obtained at several concentrations with only two independent pseudo-first-order rate constants but the linear relationship to proposed chemical rate constants is not consistent for a nontruncated system. Use of three independent pseudo-first-order rate constants does not improve the fit to experimental data and always renders the third pseudo-first-order rate constant near zero in magnitude. An optimum fit to experimental line shapes, at all relative concentrations, to within 1% deviation over at least 70 data points is obtained by the use of four independent pseudo-first-order rate constants in a truncated system. The reactions are inhibited by molecular iodine and accelerated by halide ions and a reaction mechanism involving ionization steps and unsymmetric reassociation and exchange of halogen ions with molecules is proposed. The concentration of ions is extremely low but their rate-determining control is properly demonstrated by adding iodine and halide ions in the order of 10^{-3}–10^{-2} *M* concentrations. The influence of iodine on the pseudo-first-order rate constants can be accounted for in terms of rate expressions derived from the proposed mechanism and the changes can be shown to be approximately proportional to the inverse square root of the concentration of molecular iodine which removes halide ions to form the trihalide complex ions.

Previous applications of nmr in chemical-exchange studies have mostly been directed to determination of rates in kinetic processes in which the mechanism is either known[2-8] or resolves into simple alternatives.[9-11] The few studies made to date on chemical reaction

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[1] This research was generously supported by the National Research Council of Canada in operating grants to L. W. R.

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mechanisms[12-19] by nmr were accomplished by approximate methods of line-shape analysis. We believe that the complete line-shape fitting method will provide an even more powerful means of determining the mechanism of a chemical reaction and have formulated a general approach to such problems.[20]

In the study of ^{119}Sn chemical shifts, Burke and Lauterbur[21] made an investigation of halogen exchange in mixtures of $SnCl_4$, $SnBr_4$, and SnI_4. The mixed halides were formed in a moderately rapid reaction and peaks could be identified for all mixed halides SnX_nY_{4-n}. The equilibria, as far as could be determined, represented a random redistribution of halogen atoms among the tin compounds. Nonrandom redistribution of halogen atoms and alkyl groups was also studied independently by Grant, *et al.*,[22] and Van den Berghe, *et al.*,[23] under both equilibrium and nonequilibrium conditions in reactions of R_nSnX_{4-n} compounds.

A most recent study using proton magnetic resonance by Van den Berghe, *et al.*,[24] of binary mixtures of methyltin halides shows that halogen exchange can be rapid or slow on the nmr time scale and is dependent on the particular mixed halide and on the solvent in some cases. The work is qualitative at best and some features of it are difficult to explain, especially the vast change in halogen exchange rates between chloroform and carbon tetrachloride used as solvents. A preliminary study with emphasis on purity of reactants and solvents was made of halogen exchange in binary mixtures of dimethyltin dihalides[25] and a simple mechanism was proposed for the process. At that time, the line-shape fitting procedures described in the previous paper[20] were not fully developed. It is the purpose of this study to apply the more extended theory[20] to the exchange of halogens in dimethyltin dihalide mixtures.

Experimental Section

(a) **Dimethyltin Dihalides.** Dimethyltin dichloride and dimethyltin dibromide were obtained commercially from Alfa Inorganics, Inc., and were purified by subliming *in vacuo* at room temperature. Dimethyltin diiodide was prepared from dimethyltin oxide and hydriodic acid, a more direct method to yield dimethyltin diiodide in a high state of purity. This method, different from that reported in ref 25 using tetramethyltin and tin tetraiodide, produces only the diiodide. The crude dimethyltin diiodide resulted from the reaction

$$(CH_3)_2SnO + 2HI \longrightarrow (CH_3)_2SnI_2 + H_2O$$

in aqueous medium and was colored reddish brown by the iodine usually present due to slight decomposition of the rather unstable iodide. An aqueous solution of the crude diiodide was treated with sodium thiosulfate to remove the iodine and the decolorized solution was shaken with several portions of chloroform to extract the dimethyltin diiodide. The solvent was removed from the extract by evaporation under reduced pressure and the solid dimethyltin diiodide was recrystallized from carbon tetrachloride. The crystals were dried under reduced pressure and the melting point of the colorless crystals was found to be 42°.

(b) Preparation of Nmr Samples and Their Storage. Binary mixtures of the three dimethyltin dihalides were prepared in toluene of spectro grade quality previously and permanently dried by keeping over molecular sieve. The solutions were put in standard 5-mm o.d. nmr tubes and about 1% by wt of TMS was added to give a line-shape standard. A glass-wool plug was then inserted in the upper part of the nmr tube and above it some molecular sieve (Linde 4 Å) was suspended. After that the samples were degassed by the conventional freeze–pump–thaw cycles and then sealed. The samples were always stored in the dark in a refrigerator. The above precautions were made to reduce to a minimum the presence of water or hydroxylic impurities to which the chemical exchange rates of the halogens in these systems are very sensitive and to prevent photolysis of the halides particularly the iodide.

(c) Nmr Measurements. Proton magnetic resonance measurements were obtained using a Varian HA-100 spectrometer equipped with a V-6031 variable temperature probe and temperature controller. The line width and shape in the absence of chemical exchange effects were closely watched by continually monitoring the TMS signal which was optimized to minimum line width and Lorentzian shape by careful adjustment of the homogeneity controls of the spectrometer. Spectra were recorded with field-frequency lock on the methyl peak of the solvent at a sweep rate of 0.1 Hz sec^{-1} in the approximately slow passage limit[26] with an H_1 field of 0.02 mG such conditions being well below the requirements for a nonsaturated line.[26] Intensity measurements required to determine the population at each site in the dimethyltin dihalide systems were made by repeated tracings (at least 3 per spectrum) onto good quality bond paper and cutting out the spectra for weighing of individual peaks. Overlapping of main peaks and satellites were accounted for by their relative natural abundances.

Computation and Fitting of Line Shapes

A computer program CLSFIT[27] has been written to accommodate exchange of transverse magnetization among up to 24 sites. This program computes exchange modified line shapes and iterates to optimize the complete fit of an experimental spectrum by a theoretical one. Iteration can be controlled to optimize the pseudo-first-order exchange rates, the line positions, the spin-site populations and the apparent line widths in the absence of chemical exchange.

The steady-state absorption line shape is computed from the absorption line-shape function[28]

$$Y(x) = -\mathrm{Re}\{A\boldsymbol{I}\cdot\mathbf{S}\cdot[\Lambda + (R_2 + ix\mathbf{I})]^{-1}\cdot\mathbf{S}^{-1}\cdot\boldsymbol{P}\} \quad (1)$$

where A is a scalar constant, $\boldsymbol{I}$ is a transition intensity row vector, R_2 is the transverse relaxation rate including instrumental effects in the absence of exchange, x is the

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independent frequency variable, I is a unit matrix, $\boldsymbol{P}$ is the spin-site population column vector, and $\mathbf{S}$ is the transformation matrix which diagonalizes $[\mathbf{K} - i\boldsymbol{\Omega}]$, namely

$$\boldsymbol{\Lambda} = \mathbf{S}^{-1}\cdot[\mathbf{K} - i\boldsymbol{\Omega}]\cdot\mathbf{S} \qquad (2)$$

where $\mathbf{K}$ is the rate matrix, $i = \sqrt{-1}$, and $\boldsymbol{\Omega}$ is a diagonal matrix of spin-site Larmor frequencies. The required input data are discussed in greater details in the following.

(a) **Rate Matrix K.** This is the heart of the problem. It is a square $n \times n$ matrix, where n is the number of exchange sites. As was mentioned in the first paper[20] of this series, the elements in this matrix are pseudo-first-order rate constants. The number of independent pseudo-first-order rates and the relations between them depend on whether the system in question is truncated or not. An experimental spectrum can always be fitted completely with these pseudo-first-order rates before any mechanism for the exchange process is known.

(b) Spin-Site Frequency Matrix $\boldsymbol{\Omega}$. It is diagonal with elements $\boldsymbol{\Omega}_i = (\omega_i - \omega_0)$ where ω_i is the Larmor frequency of the ith site and ω_0 is a reference frequency. These elements are generally obtained to a first approximation by observation in the slow exchange limit. The fitting routine in the program CLSFIT will automatically make fine adjustments of these values to minimize the mean error per data point in the fitting process.

(c) Spin-Site Population Vector P. The elements of this vector are equilibrium concentrations in moles per liter of each species in each site. They are determined by weighing individual nmr peaks as described in the previous section and from the known amounts of substances used in preparing the samples. The fitting routine will also make fine adjustments of these parameters, if necessary, to minimize the fit error.

(d) Transverse Relaxation Rate R_2. This rate includes all instrumental effects of magnet inhomogeneity. In all cases discussed in this work these effects are much larger than the natural relaxation rates. So in the absence of chemical exchange all resonances have the same line width defined by the line-shape standard. This parameter is also automatically adjusted when necessary by the fitting routine to give a better fit.

Analysis of Fitting Errors

The total line-shape fitting errors are expressed as the mean error per cent per data point, ϵ, given by

$$\epsilon = \frac{1}{N}\sum_{i=1}^{N}[Y^e(x_i) - Y(x_i)] \qquad (3)$$

where N is the total number of data points across the spectrum, $Y^e(x_i)$ and $Y(x_i)$ are the normalized experimental and theoretical intensities, respectively, for the frequency x_i such that

$$Y^e{}_{\max} = Y_{\max} = 100$$

Usually this error can be less than 2% except for the extreme fast and slow exchange regions where determination to 5% deviation is acceptable.

General Observations

The proton magnetic resonance spectra at 100 MHz of three binary mixtures of dimethyltin dihalides (namely, dichloride–dibromide, dichloride–diiodide, and dibromide–diiodide) at room temperature show in each case one broad peak of full width at half-maximum ranging from 5 to 15 Hz with unresolved tin-117 and tin-119 satellites. Variation of the concentrations of the components in each binary mixture from 0.4:0.6 to 0.5:0.5 and to 0.6:0.4 M shows the corresponding changes due to difference of the relative amounts of the components while the overall exchange modified spectrum is essentially the same. The exchange rates in all these mixtures are of more or less the same magnitude. These observations are quite different from those of Van den Berghe, *et al.*,[24] in that their exchange in the dimethyltin dichloride and dibromide mixture is fast, resulting in one sharp main peak and four satellites and their exchange in the dichloride–diiodide or dibromide–diiodide mixture is slow, giving a resolved or partially resolved spectrum. Such discrepancies can be explained by the following observations and will be fully accounted for quantitatively in a later section.

In our routine observation of exchange in carefully prepared and sealed samples kept under controlled conditions, it was found that over a period of 6 months samples kept in the dark in a refrigerator showed the same line shape indicating unchanged exchange rates over the period. Samples of mixtures containing the diiodide as one component, if not kept in the dark, showed considerable reduction in exchange rates on standing. The dichloride and dibromide mixture had much better keeping qualities even if stored at room temperature in the light. One sample containing the diiodide was once accidentally put close to a window; the solution was turned slightly purplish probably due to liberation of iodine by photolysis. The sample gave a well-resolved spectrum at room temperature showing a tremendous reduction in exchange rates. Experiments were performed in which varying amounts of I_2 were added to each of the three binary mixtures of the dihalides (concentrations of I_2 in the solutions ranging from 10^{-3} to 3×10^{-2} M) and pmr spectra were run. For the diiodide–dibromide and diiodide–dichloride mixtures, 10^{-3} M I_2 present in the solutions retarded the exchange sufficiently to give well-resolved spectra of three main peaks corresponding to the two symmetric dihalides and the mixed dihalide and the tin satellites. The inhibiting effect of the added I_2 tended to reach a limit when the I_2 concentration approached to about 10^{-2} M. For the dibromide–dichloride mixture exchange was also retarded by the presence of I_2 but the inhibiting effect was at least an order of magnitude smaller than in the previous two mixtures as the spectrum for this mixture was just about to resolve at I_2 concentration of 3×10^{-2} M. Denoting the inhibiting effect of iodine to halogen exchange in a binary mixture of A and B by $M_e{}^I$ (A, B) we can summarize the above observations qualitatively as $M_e{}^I$ (Me_2SnI_2, Me_2SnBr_2) slightly > $M_e{}^I$ (Me_2SnI_2, Me_2SnCl_2) ≫ $M_e{}^I$ (Me_2SnBr_2, Me_2SnCl_2).

Testing of a Proposed Mechanism

In the case of halogen exchange in a mixture of two dimethyltin dihalides, a kinetic scheme was proposed by Allan, *et al.*[25] The scheme consists of ten bimolecular reactions taking place simultaneously at their respective rates. Only four of the reactions contribute to modify the line shape of the methyl proton resonances. They are

$$(CH_3)_2SnX_2 + (CH_3)_2SnY_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(CH_3)_2SnXY \tag{4}$$

$$(CH_3)_2{}^*SnX_2 + (CH_3)_2SnXY \xrightarrow{k_2} (CH_3)_2{}^*SnXY + (CH_3)_2SnX_2 \tag{5}$$

$$(CH_3)_2{}^*SnY_2 + (CH_3)_2SnXY \xrightarrow{k_3} (CH_3)_2{}^*SnXY + (CH_3)_2SnY_2 \tag{6}$$

with specific rate constants k_1, k_{-1}, k_2, and k_3.

Naturally occurring tin has two magnetic isotopes with spin half properties and appreciable abundances, namely ^{117}Sn, 7.67%, and ^{119}Sn, 8.68%. These isotopes have similar magnetogyric ratios and their satellites on each side of the main methyl proton resonances are only about 1 Hz apart. The complete spectrum in the slow exchange limit consists of 15 peaks. Chemical exchange of the type outlined in reactions 4–6 does not involve breaking of the Sn–C bond so that the spin–spin coupling is preserved during the exchange process. This has important consequences and it has been shown[25] that, from the symmetry of the spin multiplets, the 15 × 15 problem can be simplified to five 3 × 3 similar subproblems. Correspondingly the 15 × 15 rate matrix **K** can then be partitioned into five 3 × 3 blocks identical with each other. On the basis of the proposed mechanism and in the representation of $(CH_3)_2SnX_2$, $(CH_3)_2SnXY$, and $(CH_3)_2SnY_2$, the 3 × 3 matrix $\mathbf{K}^{(s)}$ (which is to repeat up to 5 times) contains only two independent pseudo-first-order rate constants K_1 and K_2 shown in eq 7 where the

$$\mathbf{K}^{(s)} = \begin{bmatrix} K_1 & -K_1' & 0 \\ -K_1 & K_1' + K_2 & -K_2' \\ 0 & -K_2 & K_2' \end{bmatrix} \tag{7}$$

K's and K''s are related by detailed balancing. The full 15 × 15 matrix **K** can be found in ref 25.

Considering the kinetics of the reactions 4–6 the pseudo-first-order rate constants K_1 and K_2 can be formulated in terms of the specific rate constants k_1, k_{-1}, k_2, and k_3 as follows in eq 8 and 9. Thus an

$$K_1 = k_1[Me_2SnY_2] + k_2[Me_2SnXY] \tag{8}$$

$$K_2 = k_3[Me_2SnY_2] + k_{-1}[Me_2SnXY] \tag{9}$$

experimental line shape can be fitted by the use of K_1 and K_2 with a spin-site frequency matrix, $\mathbf{\Omega}$, a population vector, **P**, and an instrumental transverse relaxation rate R_2 as described before. And if the proposed mechanism is correct, eq 8 and 9 show that k_1, k_{-1}, k_2, and k_3 can be individually determined by varying the known concentrations. In principle, two samples of different relative concentrations can determine all the specific rate constants. But, in practice, in order to overdetermine the system, several samples of various relative concentrations are used to minimize experimental errors in individual measurements. Table I shows the best fit values K_1 and K_2 to within 3% errors for the binary mixture of $(CH_3)_2SnI_2$ and $(CH_3)_2SnBr_2$ at three different relative concentrations and at three different temperatures.

Table I. Best Fit K_1 and K_2 for the $(CH_3)_2SnI_2$–$(CH_3)_2SnBr_2$ Mixture

	[Me₂SnI₂] 0.176:0.448: 0.376 *M*		[Me₂SnIBr] 0.267:0.466: 0.267 *M*		[Me₂SnBr₂] 0.376:0.448: 0.176 *M*	
Temp, °C	K_1, sec^{-1}	K_2, sec^{-1}	K_1, sec^{-1}	K_2, sec^{-1}	K_1, sec^{-1}	K_2, sec^{-1}
−29.0	10.1	9.2	19.3	13.5	2.7	2.2
−34.5	8.4	7.5	16.2	11.9	2.1	1.4
−40.0	8.0	7.1	11.8	8.5	1.8	1.2

Attempts to solve for k_1, k_{-1}, k_2, and k_3 according to eq 8 and 9 using the best-fit values of K_1 and K_2 in Table I were made but without success. Thus within experimental errors the proposed mechanism turned out to be not consistent with experimental observations. Moreover, such mechanism could not explain the fact that traces of iodine considerably retard the halogen exchange while most other known impurities accelerate it extensively.

Search for an Acceptable Mechanism

Before we gave up the last proposed mechanism, attempts to fit experimental spectra with three pseudo-first-order rate constants instead of two before were made. This third rate K_3 was assumed to be zero before on the ground that there is no direct transfer of magnetization from $(CH_3)_2SnX_2$ to $(CH_3)_2SnY_2$ within the proposed scheme for the exchange of halogens. Best-fit values of K_1, K_2, and K_3 were computed. All the K_3 were very small if nonzero and K_1 and K_2 were about the same, within fitting errors, as those obtained in fits with only two pseudo-first-order rate constants. This means that no direct exchange occurs between $(CH_3)_2SnX_2$ and $(CH_3)_2SnY_2$ but the actual exchange mechanism remains to be found.

After eliminating mechanisms explainable with two or three pseudo-first-order rate constants, an attempt was then made to fit the experimental spectra with four[29] pseudo-first-order rate constants. The matrix $K^{(s)}$ is then given by[20]

$$K^{(s)} = \begin{bmatrix} D_1 & -K_3 & 0 \\ -K_1 & D_2 & -K_4 \\ 0 & -K_2 & D_3 \end{bmatrix} \tag{10}$$

where

$$D_1 = K_3[Me_2SnXY]/[Me_2SnX_2] \tag{11}$$

$$D_2 = K_1[Me_2SnX_2]/[Me_2SnXY] + K_4[Me_2SnY_2]/[Me_2SnXY] \tag{12}$$

$$D_3 = K_2[Me_2SnXY]/[Me_2SnY_2] \tag{13}$$

Fitting with four K's, unexpectedly, afforded an even better fit to within 1% with reasonable ease. The best fit values of K_1 and K_3 and K_2 and K_4 were not necessarily related. This suggested that we had a truncated system. Moreover, the best fit values of K_2 and K_3 are more accurate and very reproducible as they can be determined individually from eq 11 and 13 while those of K_1 and K_4 are less reproducible as they always appear as a weighted sum in eq 12. The weighted sum of K_1 and K_4 has the same accuracy as K_2 and K_3 but their individual values suffer from

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(29) The maximum number is six for a 3 × 3 system, but two have been established to be zero leaving four independent ones.

greater inaccuracy as was discussed in an earlier paper.[20]

A survey of the literature on chemical reactions involving organotin and halogen compounds[30-32] leads to a new kinetic scheme for the halogen exchange process. This scheme consists of four ionization steps

$$Me_2SnX_2 \underset{a_{-1}}{\overset{a_1}{\rightleftharpoons}} Me_2SnX^+ + X^- \qquad (14)$$

$$Me_2SnY_2 \underset{a_{-2}}{\overset{a_2}{\rightleftharpoons}} Me_2SnY^+ + Y^- \qquad (15)$$

$$Me_2SnXY \underset{a_{-3}}{\overset{a_3}{\rightleftharpoons}} Me_2SnX^+ + Y^- \qquad (16)$$

$$Me_2SnXY \underset{a_{-4}}{\overset{a_4}{\rightleftharpoons}} Me_2SnY^+ + X^- \qquad (17)$$

with equilibrium quotients Q_i given by

$$Q_i = a_i/a_{-i} \quad (i = 1, 2, 3, \text{and } 4) \qquad (18)$$

and two unsymmetric halogen transfer steps

$$Me_2SnX_2 + Y^- \underset{b_{-1}}{\overset{b_1}{\rightleftharpoons}} Me_2SnXY + X^- \qquad (19)$$

$$Me_2SnY_2 + X^- \underset{b_{-2}}{\overset{b_2}{\rightleftharpoons}} Me_2SnXY + Y^- \qquad (20)$$

Calculations from electric dipole moment data of organotin halides show that the Sn–C bond is mainly covalent whereas the Sn–X bond has >27% ionic character.[33,34]

Electric conductance experiments[35-37] showed that organotin halides did ionize in aprotic organic solvents though not to a very great extent. It will be shown later that these steps are quite important in the rate determining though their direct contribution to the overall exchange rates is much smaller than that from the unsymmetric halogen transfer steps (19 and 20). Halogen exchange reactions involving halides and halide ions have been very extensively studied.[38] Reactions such as 19 and 20 involving organotin compounds may possibly take place *via* the pentacoordinate tin complex as the intermediate state.[39]

In the above kinetic scheme all the six two-way reactions are rate determining and contribute to modify the nmr line shape. Apart from these, four reactions (eq 21–24) may also take place at the same time. These

$$Me_2SnX_2 + {}^*X^- \xrightarrow{b_3} MeSnX^*X + X^- \qquad (21)$$

$$Me_2SnY_2 + {}^*Y^- \xrightarrow{b_4} Me_2SnY^*Y + Y^- \qquad (22)$$

$$Me_2SnXY + {}^*X^- \xrightarrow{b_5} Me_2Sn^*XY + X^- \qquad (23)$$

$$Me_2SnXY + {}^*Y^- \xrightarrow{b_6} Me_2SnX^*Y + Y^- \qquad (24)$$

reactions are symmetric in the halogen exchanged and no modulation of the methyl proton resonances occurs.

On the basis of the above kinetic scheme, consideration of the rate of formation of each dihalide leads to the following relations between the pseudo-first-order rate constants K_{1-4} and specific constants a's and b's.[40]

$$K_1 = a_3([XY]/[X_2]) + b_1[Y^-] \qquad (25)$$

$$K_2 = a_2([Y_2]/[XY]) + b_{-2}[Y^-] \qquad (26)$$

$$K_3 = a_1([X_2]/[XY]) + b_{-1}[X^-] \qquad (27)$$

$$K_4 = a_4([XY]/[Y_2]) + b_2[X^-] \qquad (28)$$

The effects of iodine in retarding the exchange are explained by reactions 29 and 30 by which the concentrations of X^- and Y^- are considerably reduced.

$$I_2 + X^- \rightleftharpoons I_2X^- \qquad C_1 = \frac{[I_2X^-]}{[I_2][X^-]} \qquad (29)$$

$$I_2 + Y^- \rightleftharpoons I_2Y^- \qquad C_2 = \frac{[I_2Y^-]}{[I_2][Y^-]} \qquad (30)$$

Using the detailed balancing of charged species in the solution of the mixture of dimethyltin dihalides and some iodine, expressions for the equilibrium concentrations of X^- and Y^- are obtained (eq 31 and 32).

$$[X^-] = \frac{Q_1[X_2] + Q_4[XY]}{\{(Q_1[X_2] + Q_4[XY])(1 + C_1[I_2]) + (Q_2[Y_2] + Q_3[XY])(1 + C_2[I_2])\}^{1/2}} \qquad (31)$$

$$[Y^-] = \frac{Q_2[Y_2] + Q_3[XY]}{\{(Q_1[X_2] + Q_4[XY])(1 + C_1[I_2]) + (Q_2[Y_2] + Q_3[XY])(1 + C_2[I_2])\}^{1/2}} \qquad (32)$$

From these equations it is obvious that if either or both of $C_1[I_2]$ and $C_2[I_2]$ is much larger than 1 the $[X^-]$ and $[Y^-]$ will be much reduced. It is also important to note that the system under study based on this reaction scheme is a truncated system as some of the species, namely the Me_2SnX^+ and Me_2SnY^+, involved in the reactions are not observable under the highest gain conditions of the Varian HA-100 nmr spectrometer.

Additional Experiments and Results

The three following experiments were specifically designed to verify the above reaction scheme.

(a) Variation of Best-Fit Pseudo-First-Order Rate Constants K_2 and K_3 with Iodine Concentration. Pmr spectra of the binary mixture of dimethyltin diiodide and dimethyltin dibromide (initial concentration of components: 0.6 *M* diiodide and 0.4 *M* dibromide) at 29.5° with iodine concentrations ranging from 0 to 10^{-2} *M* were taken. Complete line-shape fitting with four *K*'s was made to within 2% errors. Their best fit values are shown in Table II and K_2 and K_3 (which have been shown to be individually determinable and very reproducible) are plotted against $1/[I_2]^{1/2}$ in Figure 1. Typical fits of experimental and theoretical spectra are shown in Figures 2 and 3 for the mixture of dimethyltin diiodide (0.6 *M*) and dimethyltin dibromide (0.4 *M*) in toluene at 29.5° without and with 5×10^{-3} *M* I_2, respectively.

By comparing the best-fit exchange rates in mixtures with and without I_2 one can say that the first terms in eq 25–28 which are not affected by I_2 are very

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(30) (a) A. K. Sawyer, Ed., "Organotin Compounds," Vol. I–III, Marcel Dekker, New York, N. Y., 1971; (b) W. P. Neumann, "Organic Chemistry of Tin," Interscience, London, 1970.

(31) R. C. Poller, "Chemistry of Organotin Compounds," Logos Press, London, 1970.

(32) V. Gutmann, Ed., "Halogen Chemistry," Vol. I–III, Academic Press, New York, N. Y., 1967.

(33) C. P. Smyth, *J. Org. Chem.*, **6**, 421 (1941).

(34) C. P. Smyth, *J. Amer. Chem. Soc.*, **63**, 57 (1941).

(35) C. A. Kraus and C. C. Callis, *ibid.*, **45**, 2624 (1923).

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(37) R. Schick, Ph.D. Dissertation, University of Giessen, 1965.

(38) Reference 32, Vol. I, p 41.

(39) Reference 30b, p 14, and references quoted therein.

(40) [XY] = [Me_2SnXY], etc.

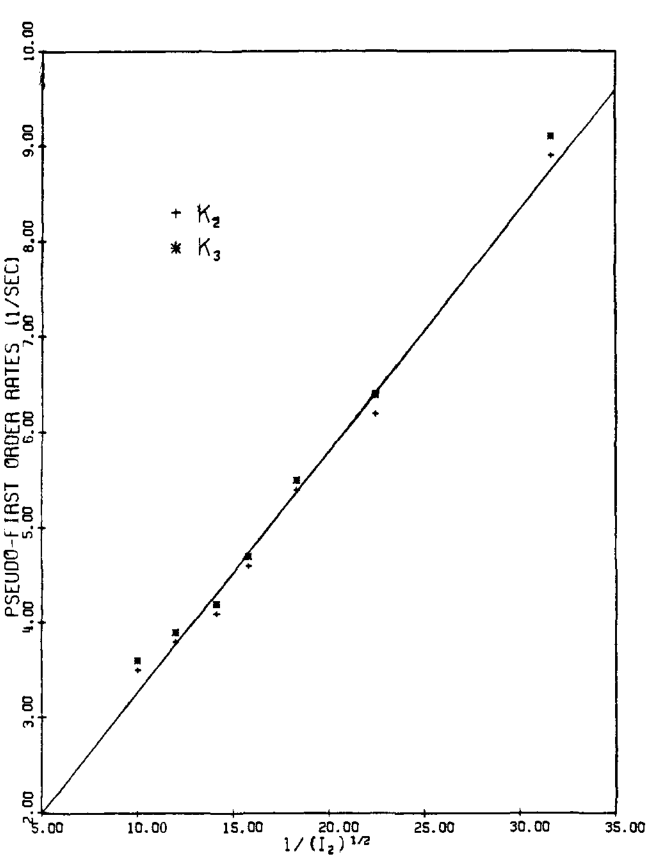

Figure 1. Plot of pseudo-first-order rate constants *vs.* iodine concentrations.

Table II. Best-Fit Pseudo-First-Order Rate Constants in Binary Mixture of Dimethyltin Diiodide and Dibromide with I_2 at 29.5°

Best-fit rate constants, sec^{-1}				Iodine concn	
K_1	K_2	K_3	K_4	$[I_2] \times 10^3$, mol/l.	$1/[I_2]^{1/2}$, mol$^{-1/2}$ l.$^{1/2}$
275.0	220.0	230.0	570.0	0	∞
10.8	8.9	9.1	22.6	1	31.6
7.6	6.2	6.4	15.8	2	22.4
6.6	5.4	5.5	13.8	3	18.3
5.6	4.6	4.7	11.7	4	15.8
4.9	4.1	4.2	9.9	5	14.1
4.4	3.8	3.9	9.0	7	12.0
3.9	3.5	3.6	8.1	10	10.0

much smaller than the second terms when $[I_2] = 0$. Traces of I_2, 10^{-3} *M*, are sufficient to reduce the latters by more than an order of magnitude. $[I_2]$ about 10^{-2} *M* already reduces the second terms to about the same as or even smaller than the first terms. From eq 26, 27, 31, and 32 if $C_1[I_2] \approx C_2[I_2] \gg 1$ or $C_1[I_2] \gg C_2[I_2] \gg 1$ is satisfied, K_2 and K_3 are approximately proportional to $1/[I_2]^{1/2}$. This is borne out by the approximate linear plot in Figure 1.

(b) Effects of Added Halide Ions on the Exchange. Most tetraalkylammonium halides are quite insoluble in toluene, the solvent used in our exchange studies. Tetrabutylammonium bromide was found to be most convenient and dissolves to somewhat above 10^{-3} *M* in neat dry toluene. This compound was also found to dissolve much more readily in toluene containing the dimethyltin dihalides to more than 10^{-2} *M*. Pure dry tetrabutylammonium bromide (mol wt 322.38) was added by the mg to 1 ml of the solution of the equimolar mixture (0.5:0.5 *M*) of dimethyltin dibromide and dichloride. The solution was well equilibrated and nmr spectra were run at 29.5°. One milligram of $(C_4H_9)_4NBr$ in 1 ml gives a concentration of 3.1×10^{-3} *M* Br^- ion if the salt ionizes completely. There is no information about the extent of ionization under our experimental conditions so the following observations are only qualitative. Approximate pseudo-first-order rate constants K_2 and K_3 were about 100 sec^{-1} in the neat mixture without $(C_4H_9)_4NBr$. With 1 mg of the salt added the previously collapsed broad peak sharpened up considerably giving K_2 and K_3 approximately 3000 sec^{-1}. Further addition of 1 mg of the salt approximately doubled the effects. This observation verified eq 26 and 27 qualitatively. Accuracy in determination of exchange rates is relatively low in this extremely fast exchange limit. An upper limit for the concentration of ions from the ionization steps is derived to be 10^{-4} *M* by comparing the exchange rates with and without $(C_4H_9)_4NBr$ added.

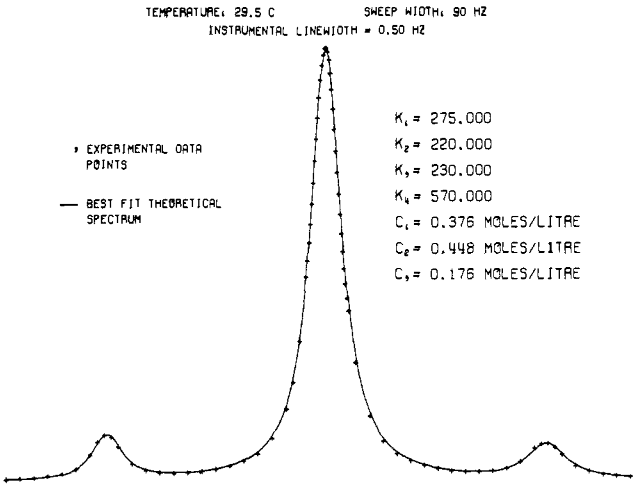

Figure 2. Pmr best fit experimental and theoretical spectra for the dimethyltin diiodide–dimethyltin dibromide mixture without iodine.

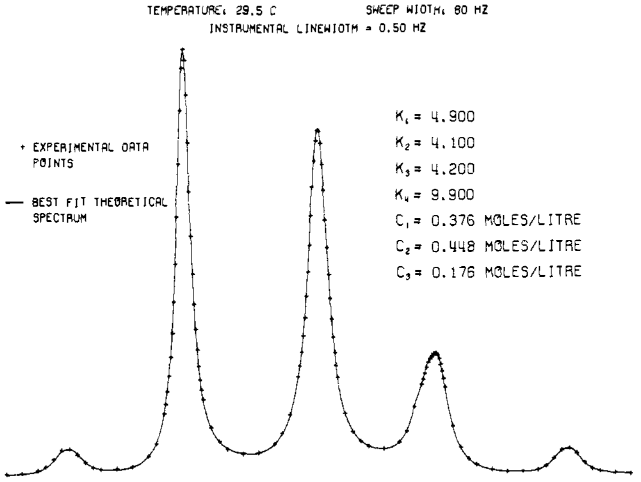

Figure 3. Pmr best fit experimental and theoretical spectra for the dimethyltin diiodide–dimethyltin dibromide mixture with 0.005 *M* iodine.

(c) Variation of Exchange Rates K_2 and K_3 with

$(C_4H_9)_4NBr$ Concentration in the Presence of 2×10^{-2} M I_2. A 1 ml solution containing 0.6 mmol $(CH_3)_2SnI_2$, 0.4 mmol $(CH_3)_2SnBr_2$, and 2×10^{-2} mmol of I_2 was first prepared in pure dry toluene and a pmr spectrum of it was taken at 29.5°. Successive amounts of 1 mg each of $(C_4H_9)_4NBr$ were added and the equilibrated sample was rerun for a spectrum for five times. Complete line-shape fitting of the spectra was made to within 3% errors. The best-fit values of K_2 or K_3 were plotted against the amount of $(C_4H_9)_4NBr$ added in Figure 4. The approximate equality of K_2 and K_3 was only accidental. The plot in Figure 4 shows an approximately linear but small increase in rates as more $(C_4H_9)_4NBr$ is added at the beginning when the total amount of $(C_4H_9)_4NBr$ added is much smaller than the amount of I_2 present in the solution. The plot then curves up more and more rapidly as the total amount of $(C_4H_9)_4NBr$ added becomes larger and comparable to the initial amount of I_2. This behavior is in agreement with the theory based on the proposed reaction scheme. The I_2 when present in excess over the Br^- added ties down most of the Br^- added as I_2Br^- allowing only a slow increase in the Br^- and I^- concentrations. When the Br^- added becomes comparable to the initial amount of I_2 present in the solution, the reaction

$$I_2 + Br^- \rightleftharpoons I_2Br^-$$

removes an appreciable amount of the molecular I_2 leaving the equilibrium concentration of I_2 lower and lower as more and more of the bromide is added. $[I_2]$ appears in the denominator part of the fraction in eq 31 and 32. Its getting smaller and smaller makes the Br^- and I^- concentrations larger and larger more rapidly. This accounts for the more rapid increase in the exchange rates in the later part of the plot in Figure 4.

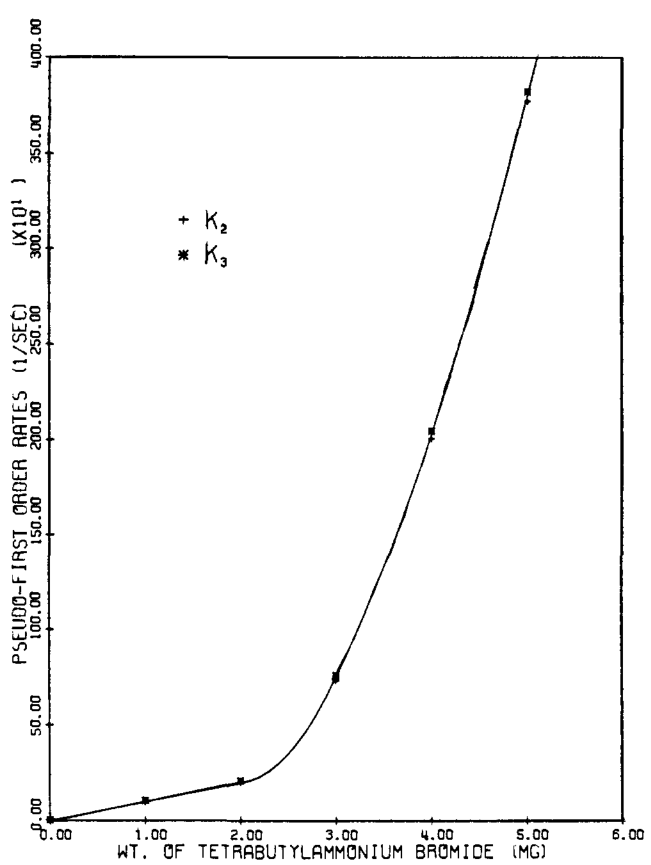

Figure 4. Plot of pseudo-first-order rates *vs.* weight of tetrabutylammonium bromide.

Discussion and Conclusion

In this work it is shown that the nmr technique is a more powerful tool than the conventional methods to study chemical reactions. It not only affords easy determination of equilibrium and nonequilibrium reaction rates but also provides a means of detailed determination of reaction mechanisms.

In the organotin halide systems, exchange reactions can take place in three ways, involving either (a) breaking and forming of only Sn–X bonds, (b) breaking and forming of only Sn–C bonds, or (c) breaking and forming of both Sn–X and Sn–C bonds.

In the present study of the dimethyltin dihalide systems by nmr, the breaking and forming of Sn–C bonds is ruled out by readily available evidence from a pmr spectrum of the methyl proton resonances, namely that there is no tendency of the tin satellites collapsing into the main peaks even in the extremely fast exchange limit. Moreover, the verified conclusion that there is no direct transfer of magnetization from Me_2SnX_2 to Me_2SnY_2 reconfirms the above ruling. It has also been shown[22,23] that at temperatures below 50° exchange reactions involving breaking and forming of Sn–X and Sn–C bonds in dimethyltin dihalide are energetically unfavorable. So under the experimental conditions the reaction in the dimethyltin dihalide systems involves only halogen exchange and the mechanistic scheme consists of four ionization steps and two halogen transfer steps possibly *via* the pentacoordinate tin intermediate. The inhibiting properties of I_2 to halogen exchange in these systems are due to formation of complex trihalide ions of the type I_2X^-. The observed sequence M_e^I (Me_2SnI_2, Me_2SnBr_2) slightly > M_e^I (Me_2SnI_2, Me_2SnCl_2) ≫ M_e^I (Me_2SnBr_2, Me_2SnCl_2) is consistent with the stability constant data of Benoit and Guay[41] for I_3^-, I_2Br^-, and I_2Cl^- in aprotic solvents.

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