Hydrogen-1 Nuclear Magnetic Resonance Study of Halogen Exchange between Trimethyltin Halides in Solution

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The kinetics of halogen exchange in binary mixtures of trimethyltin halides in solution have been investigated by total line-shape analyses of their ^{1}H n.m.r. spectra. The results obtained for solvents of different permittivities allows a distinction to be made between an associative or dissociative mechanism and it is concluded that ionization does play a part in the kinetics.

It has been demonstrated by ^{1}H n.m.r. spectroscopy that facile halogen exchange occurs in binary mixtures of methyltin halides and that the rate of exchange depends on the particular mixed-halide system and on the solvent.[1] A detailed ^{1}H n.m.r. line-shape study of some of these systems in toluene solution has recently been made by Chan and Reeves [2] who concluded that ionization of the methyltin halide was an essential prerequisite to halogen exchange. In another study of the same system in the same solvent Peregudov *et al.*[3] argued that such an ionization was untenable in an aprotic solvent like toluene and proposed that the exchange mechanism was an associative one involving a five-coordinate bridged intermediate.

We now comment on these conflicting viewpoints in the light of our own studies of these systems in different solvents.

EXPERIMENTAL

Materials.—Trimethyltin chloride and bromide were obtained from Ralph N. Emanuel Ltd. The chloride was purified by vacuum sublimation and the bromide by fractional distillation under reduced pressure. Trimethyltin iodide was prepared in two ways. First by the reaction between tin(IV) and methylmagnesium iodide. Tin(IV)

$$\mathrm{SnI_4 + 3MgMeI \longrightarrow [SnMe_3I] + 3MgI_2} \qquad (1)$$

iodide (0.1 mol) and diethyl ether (100 cm^3, previously dried over sodium wire) were placed in a three-necked flask fitted with a dropping funnel and a Drikold–acetone condenser. A diethyl ether solution of methylmagnesium iodide (1.3 mol) was introduced into the dropping funnel

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[1] E. V. Van den Berghe, G. P. Van der Kelen, and Z. Eeckhaut, *Bull. Soc. chim. belges*, 1967, **76**, 79.

[2] S. O. Chan and L. W. Reeves, *Inorg. Chem.*, 1973, **12**, 1704.

[3] A. S. Peregudov, L. A. Fedorov, D. N. Kravtsov, and E. M. Rokhlina, *Zhur. obshchei Khim.*, 1972, **42**, 2194.

and the apparatus was flushed with argon. The Grignard reagent was then added dropwise over a period of 1 h while the SnI_4 was stirred with a magnetic stirrer. When the addition was complete the mixture was heated under reflux for 2 h when all the volatile products were distilled off and collected. The residue in the flask was carefully hydrolyzed with a minimum of water (violent initial reaction) and then repeatedly extracted with diethyl ether. The combined distillate and extracts was dried over anhydrous magnesium sulphate and then fractionally distilled, initially at atmospheric pressure (diethyl ether) and then under reduced pressure (products). Trimethyltin iodide distilled as a clear colourless liquid [b.p. 434 K (lit. 443 K,[4,5] 433—443 K;[6,7] m.p. 276.0—276.5 K (lit. 276.4 K,[4,5,8] 268—170 K[6,7])] while a small quantity of dimethyltin di-iodide crystallized in the condenser. The second method involved the metathetical reaction (2) in liquid sulphur dioxide.

$$[SnMe_3Cl] + KI \longrightarrow [SnMe_3I] + KCl\downarrow \qquad (2)$$

Trimethyltin iodide turns red on prolonged standing in daylight. This colouration was removed by shaking with mercury and the iodide was redistilled before use.

Tin(IV) iodide was prepared by the reaction of sublimed iodine with an excess of granulated tin in the presence of a small amount of carbon disulphide. The orange crystalline product was purified by recrystallization from benzene (m.p. 416.8 K). The solvents methylene dichloride and deuteriochloroform were obtained commercially and were distilled and stored over molecular sieves (type 4A) before use.

Arrhenius and Eyring activation parameters for the exchanges [a]

System	Solvent	Total halide concentration mol l^{-1}	T/K	$E^{\ddagger}$/kJ mol^{-1}	A	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
Cl–I	Toluene [b]	0.3	203.2—303.2	9.5 ± 0.4	8.54×10^3	7.5 ± 0.4	-171 ± 2	58.3 ± 0.2
Cl–I	CH_2Cl_2	0.2146	215.0—305.5	17.1 ± 0.3	4.05×10^6	14.9 ± 0.3	-120 ± 1	50.5 ± 0.2
Cl–I	$CDCl_3$	0.2502	199.0—300.9	12.0 ± 0.4	2.87×10^5	10.1 ± 0.1	-141 ± 1	52.1 ± 0.0
Br–I	CH_2Cl_2	0.2500	207.0—303.0	16.0 ± 0.3	1.11×10^6	16.0 ± 0.0	-121 ± 1	52.0 ± 0.0
Br–I	$CDCl_3$	0.3100	214.5—300.0	10.5 ± 0.8	4.77×10^4	11.0 ± 0.0	-143 ± 1	53.8 ± 0.0

[a] Errors quoted are least-squares errors. [b] Values computed from data in ref. 3.

Sample Preparation.—It was necessary to ensure that all the equipment used was absolutely clean and dry since small amounts of impurity had large effects on the appearance of the ^1H n.m.r. spectra. The sample tubes were first cleaned with hot concentrated chromic acid and then washed with deionized water followed by alcohol and dry diethyl ether. They were subsequently dried at 393 K. The criterion of cleanliness was that the ^1H n.m.r. spectra were reproducible. For each system examined, weighed amounts of the appropriate halides were dissolved in known weights of solvent and the required volumes of each solution were combined to give a sample of known composition. Subsequent dilution (w/w) provided a series of samples of known composition.

Spectra and Spectral Analysis.—^1H N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer as described previously.[9] A sweep time of 250 s over a sweep width of 100 Hz was used in most cases. For each binary mixture of halides the ^1H n.m.r. spectrum in the absence of exchange consisted of two absorption peaks each with two sets of satellites arising from spin–spin coupling with the nuclei ^{117}Sn and ^{119}Sn (spin $\frac{1}{2}$) which have natural abundances of 7.67 and 8.68% respectively. Since these satellites remained well resolved up to the fast-exchange limit, the rate of breaking and forming of Sn–C bonds in the system is negligible and the problem reduces to a two-site exchange repeated with appropriate intensity adjustments five times.

If in the exchange process one of the tin atoms can be labelled (*) at any instant [equation (3)], then the rate of disappearance of [*$SnMe_3X$] is given by (4) since [$SnMe_3Y$] is

$$[{}^*SnMe_3X] + [SnMe_3Y] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [{}^*SnMe_3Y] + [SnMe_3X] \qquad (3)$$

$$-\mathrm{d}\,[{}^*SnMe_3X]/\mathrm{d}t = k_2[SnMe_3Y][{}^*SnMe_3X] = k_1[{}^*SnMe_3X] \qquad (4)$$

constant; k_1 is therefore a pseudo-first-order rate constant. Experimentally, the exchange of magnetization between two sites A and B is described by the extended Gutowsky and Holm equation[9] in terms of the chemical-shift difference $\delta\omega$, the site populations p_A and p_B, and the life-times τ_A and τ_B at each site. The latter can be determined from the observed ^1H n.m.r. line shape by an iterative computer-fitting procedure and the problem is simplified (and most sensitive to the rate of exchange) when the populations p_A and p_B are equal. These conditions have been employed in this work and the lifetimes τ_A determined at each temperature are then related to k_1 and the solute concentration by equation (5). Subsequently some of the results were

$$\tau_A^{-1} = k_1[{}^*SnMe_3X] \qquad (5)$$

checked using the multiple-site exchange program POLY based on the program CLSFIT of Chan and Reeves.[10]

RESULTS

In the system [$SnMe_3Cl$]–[$SnMe_3Br$] one sharp resonance signal with accompanying satellites was observed in the ^1H n.m.r. spectrum for the full range of temperatures and concentrations employed. The coalescence temperature must therefore be significantly less than 190 K and an upper limit of *ca.* 1 kJ mol^{-1} can be applied to the activation energy of the exchange. In each of the other binary systems studied

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[4] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' 3rd edn., Methuen, London, 1967, vol. 1.

[5] 'Handbook of Chemistry and Physics,' Cleveland Rubber Co., 49th edn.

[6] R. C. Poller, 'The Chemistry of Organotin Compounds,' Logos Press, London, 1970.

[7] A. C. Smith, jun., and E. G. Rochow, *J. Amer. Chem. Soc.*, 1953, **75**, 4103.

[8] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, **60**, 459.

[9] V. I. P. Jones and J. A. Ladd, *Trans. Faraday Soc.*, 1970, **66**, 2948.

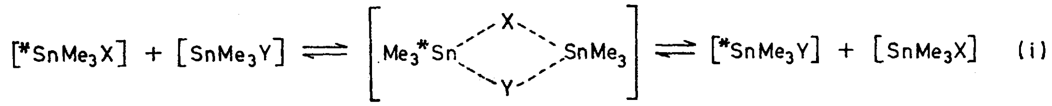
[10] S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, 1973, **95**, 673.

the rate of exchange was slower and decoalescence of the spectrum occurred below 273 K. For a given concentration in the same solvent, the rates were in the order Cl^{-}–I^{-} > Br^{-}–I^{-}. In no case was it possible to detect an additional signal from a transition state, even at the highest gain of the spectrometer.

The Arrhenius and Eyring activation parameters obtained from the temperature-dependence studies are given in the Table while the Figure shows the dependence of the rate on the product of the concentrations of the solutes, the two halides always having equal concentrations. The linearity of the latter plots at low concentrations demonstrates that the exchange kinetics are second order.

DISCUSSION

Two basic mechanisms have been proposed to explain the kinetics of halogen exchange in these systems. The first is associative involving a five-co-ordinate bridged intermediate,[3] a structure which is well documented in co-ordination compounds of tin. Such a transition state would be sensitive to the relative sizes of X and Y: the larger their radii the more difficult would the structure be to form. On purely steric grounds one would therefore predict that the bromide–iodide system should exhibit the slowest rate of exchange. Furthermore, from a thermodynamic point of view, the formation of a bridged intermediate is expected to involve a negative entropy change. Our results are in agreement with these predictions. In each case a large negative value of $\Delta S^{\ddagger}$ has been determined, while the large values of $\Delta G^{\ddagger}$ explain why the population of the transition state is undetectable experimentally.



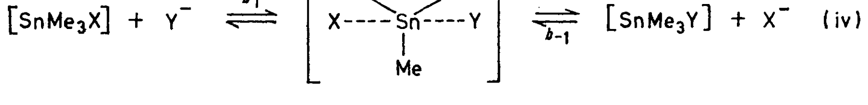
$$[{}^{*}SnMe_3X] + [SnMe_3Y] \rightleftharpoons \left[Me_3{}^{*}Sn \begin{smallmatrix} X \\ Y \end{smallmatrix} SnMe_3 \right] \rightleftharpoons [{}^{*}SnMe_3Y] + [SnMe_3X] \qquad (i)$$

$$[SnMe_3X] \underset{a_{-1}}{\overset{a_1}{\rightleftharpoons}} [SnMe_3]^{+} + X^{-} \qquad (ii)$$

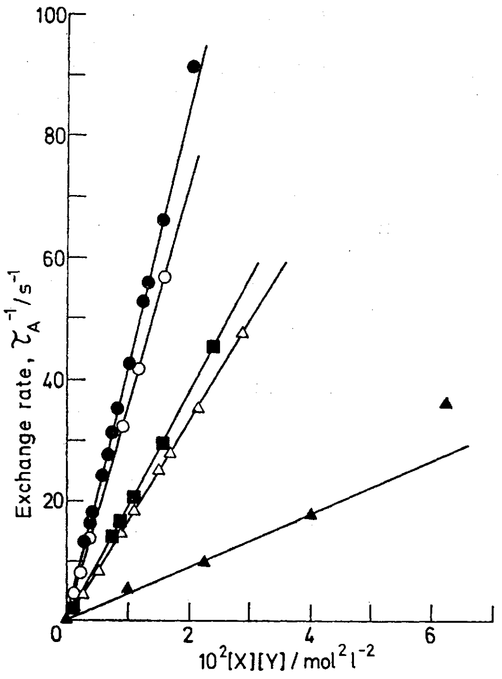
$$[SnMe_3X] \underset{a_{-2}}{\overset{a_2}{\rightleftharpoons}} [SnMe_3]^{+} + Y^{-} \qquad (iii)$$

The alternative mechanism for the halide exchange advocated by Chan and Reeves[2] involves dissociation of the tin–halogen bond followed by reaction (iv). On this basis, the pseudo-first-order rate constant k_1 may be written in terms of the specific rate constants as in (6).

$$k_1 = (a_2[SnMe_3X]/[SnMe_3X]) + b_1[Y^{-}] \qquad (6)$$



$$[SnMe_3X] + Y^{-} \overset{b_1}{\rightleftharpoons} \left[X\text{----}\underset{Me}{\overset{Me\quad Me}{Sn}}\text{----}Y \right] \underset{b_{-1}}{\rightleftharpoons} [SnMe_3Y] + X^{-} \qquad (iv)$$



Plots of exchange rates against the product of the solute concentrations for the binary systems Cl–I and Br–I in different solvents: (●), Cl–I in CH_2Cl_2 at 303 K; (○), Cl–I in $CDCl_3$ at 303 K; (▲), Cl–I in C_7H_8 at 300 K (from ref. 3); (■), Br–I in CH_2Cl_2 at 303 K; and (△), Br–I in $CDCl_3$ at 303 K

If reaction (iv) is the rate-determining step (*i.e.* $a_2 \ll b_1$), this mechanism also involves a negative $\Delta S^{\ddagger}$.

The question therefore arises whether ionization of the trialkyltin halide does occur in solution. Prince[11] stated that a necessary condition for such an ionization is the presence of an electron donor and the extent of ionization depends on the nature of the alkyl and halide groups. Conductivity measurements have shown that for solutions of alkyltin halides in aprotic solvents the values are so small that these could be due to impurities.[12] Nevertheless only a slight amount of ionization is required for this mechanism to proceed.

Chan and Reeves did not investigate the kinetics of these binary exchange systems as such but based their conclusions on an interpretation of the effect of added molecular iodine on the exchange. For small amounts of iodine ($\ll$ 0.1M) * the observed halogen-exchange rate was substantially reduced but at higher concentrations the rate was accelerated in a manner characteristic of other electron-donor impurities. The reduction in the

* 1M = 1 mol dm^{-3}.

[11] R. H. Prince, *J. Chem. Soc.*, 1959, 1783.

[12] A. B. Thomas and E. G. Rochow, *J. Inorg. Nuclear Chem.*, 1957, **4**, 205.

rate of exchange was considered to be the result of a decrease in the concentration of free halide ion X^- due to equilibrium (7). Benoit and Guay[13] reported the

$$I_2 + X^- \rightleftharpoons [I_2X]^- \quad (7)$$

formation constants (log β) of 6.5 and 4.8 for $[I_2Br]^-$ and $[I_2Cl]^-$ respectively in the aprotic solvent sulpholane.

If ionization is a prerequisite for the exchange, the nature of the solvent may be expected to influence the kinetics. For a reaction between an ion and a neutral molecule the electrostatic effects are small. The rate constant b_1 is expected to be somewhat greater in a medium of lower permittivity, but this is only true if the ionic radii are the same in each solvent. Nevertheless, even if the specific rate constants a_i are the same in each solvent, ionization is expected to be more prevalent in a solvent of high permittivity. This would be reflected in an increase in the pseudo-first-order rate constant k_1. If, however, the mechanism is as associative as advocated by Peregudov *et al.*,[3] the influence of the solvent is not expected to have a marked effect on k_1. Examination of the results in the Figure shows that k_1 does increase on going from toluene to chloroform to dichloromethane, in the order of increasing permittivity. There is not a good correlation between ln k_1 and ε^{-1} but this is not uncommon for different solvents. The results therefore support the mechanistic scheme of Chan and Reeves rather than the associative one of Peregudov *et al.*

[5/715 *Received, 15th April,* 1975]

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[13] R. L. Benoit and M. Guay, *Inorg. Nuclear Chem. Letters,* 1968, **4**, 215.