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Preliminary communication

Halogen exchange in trimethyltin halides. An inverse temperature-rate relationship

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In a semi-quantitative study[1] of halogen exchange in methyltin halides by Van den Berghe *et al.* it was shown that the exchange rates are within or near the time scale that is suitable for kinetic studies by NMR line shape analysis.

We undertook a detailed kinetic study of these exchange reactions with the long term aim of establishing the connection between the mechanism of halogen exchange and that of inversion of configuration about the tin atom in triorganotin halides. The rate of inversion was shown[2] to be also in the range of the NMR time scale; as with the rate of halogen exchange, it increases with increasing concentration of the substrate.

In order to establish the use of the NMR kinetic method for organotin halogen exchanges we first studied the iodide–bromide exchange between trimethyltin iodide (I) and trimethyltin bromide (II) in cyclohexane solution. Cyclohexane was chosen as a solvent of low nucleophilicity as well as of low polarity in order to eliminate as far as possible, the complications of ionization and of complex formation.

Although the study of this simple model system cannot in itself establish the relation between exchange and inversion, our preliminary results reveal some unexpected features of the exchange reaction.

The chemical shift difference between the methyl protons of I and II in the concentration range of 0.10–0.50 M is 0.14 ± 0.01 ppm (for I $\delta = 0.725 \pm 0.005$ ppm. $J(^{117}\text{Sn–C–H}) = 56.2 \pm 0.4$ Hz, $J(^{119}\text{Sn–C–H}) = 58.8 \pm 0.3$ Hz and for II $\delta = 0.585 \pm 0.005$ ppm, $J(^{117}\text{Sn–C–H}) = 57.2 \pm 0.2$ Hz and $J(^{119}\text{Sn–C–H}) = 59.6 \pm 0.5$ Hz).

A line shape analysis[★] of the experimental NMR spectra of mixtures with different concentration of I and II yielded values of the mean life time τ from which the life times of the individual species, τ_1 for I and τ_2 for II, were obtained. $\tau_1 = \tau/(1-P_1)$ and $\tau_2 = \tau/(1-P_2)$ where P_1 and P_2 are the fractional populations of I and II respectively.

[★] Line shapes were calculated on a CDC 6600 computer connected to a calcomp plotter. The program GMW developed by George M. Whitesides was used[3].

In order to analyse the τ values obtained we assumed the following rate equation for the exchange reaction:

$$\text{Rate} = k'[\mathrm{I}]^{\alpha}[\mathrm{II}]^{\beta} \qquad (1)$$

From the definition of τ_1, τ_2 and τ

$$\frac{1}{\tau_1} = \frac{\text{Rate}}{[\mathrm{I}]} \; ; \; \frac{1}{\tau_2} = \frac{\text{Rate}}{[\mathrm{II}]} \qquad (2)$$

and

$$\text{Rate} = \frac{1}{\tau} \; \frac{[\mathrm{I}]\,[\mathrm{II}]}{[\mathrm{I}] + [\mathrm{II}]} \qquad (3)$$

from Eq.1 and 2

$$\frac{1}{\tau_1} = k'\,[\mathrm{I}]^{\alpha-1}\,[\mathrm{II}]^{\beta} \text{ and } \frac{1}{\tau_2} = k'\,[\mathrm{I}]^{\alpha}\,[\mathrm{II}]^{\beta-1} \qquad (4)$$

The partial order β can then be obtained as the slope of the plot of log $(1/\tau_1)$ against log [II] for a series of solutions in which [II] is varied and [I] kept constant. Similarly, α is obtained from the plot of log $(1/\tau_2)$ against log [I]. Table 1 lists the partial orders α and β and the apparent rate constants k' obtained from a least squares analysis of the rate data according to the above described procedure.

TABLE 1

PARTIAL ORDERS FROM LEAST SQUARES ANALYSIS

Temperature (°C)	α	β	log k'
33	1.5 ± 0.2	2.6 ± 0.3	3.4 ± 0.2
63	1.5 ± 0.3	1.8 ± 0.1	2.9 ± 0.2
95	1.9 ± 0.2	1.8 ± 0.1	2.5 ± 0.2

Most noteworthy is the inverse temperature-rate relation as indicated by a decrease of k' with increasing temperature. This relation is not dependent on the mechanism assumed for the kinetic analysis and is apparent from a simple inspection of the spectra. Figure 1 shows the experimental and simulated spectra of a solution with [I] = 0.167 and [II] = 0.250 moles·liter^{-1}. The peaks corresponding to I and II are coalesced at 33°, but at 63° (δ_{obs} = 7.2 Hz) and at 95° (δ_{obs} = 7.8 Hz) are clearly separated

The apparent fractional orders obtained by assuming the simple kinetics of Eq.1 indicate a more complex kinetics, most probably a series of additive terms with different values of the partial orders (Eq.5). Each term in the series may represent a complex

$$\text{Rate} = \sum_i k_i'\,[\mathrm{I}]^{\alpha_i}\,[\mathrm{II}]^{\beta_i} \qquad (5)$$

reaction of consecutive steps and the decrease of the apparent rate constant with increasing temperature strongly suggests that exchange is preceded by various association

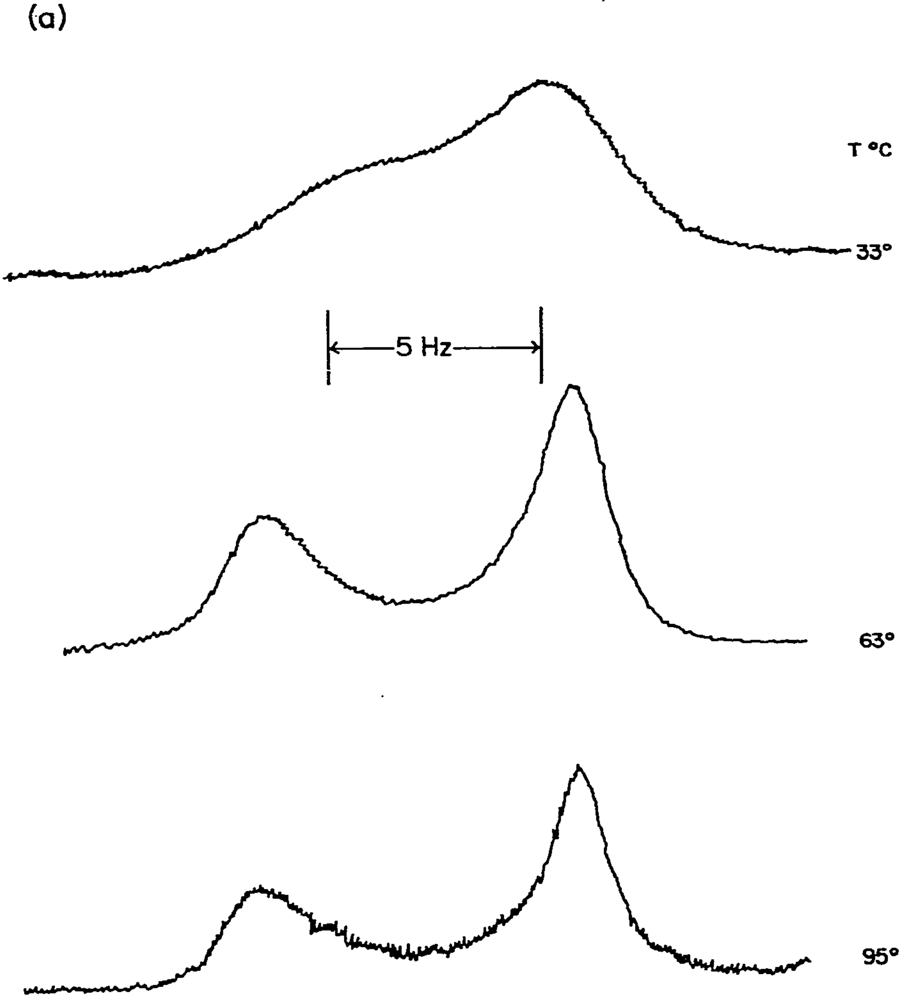
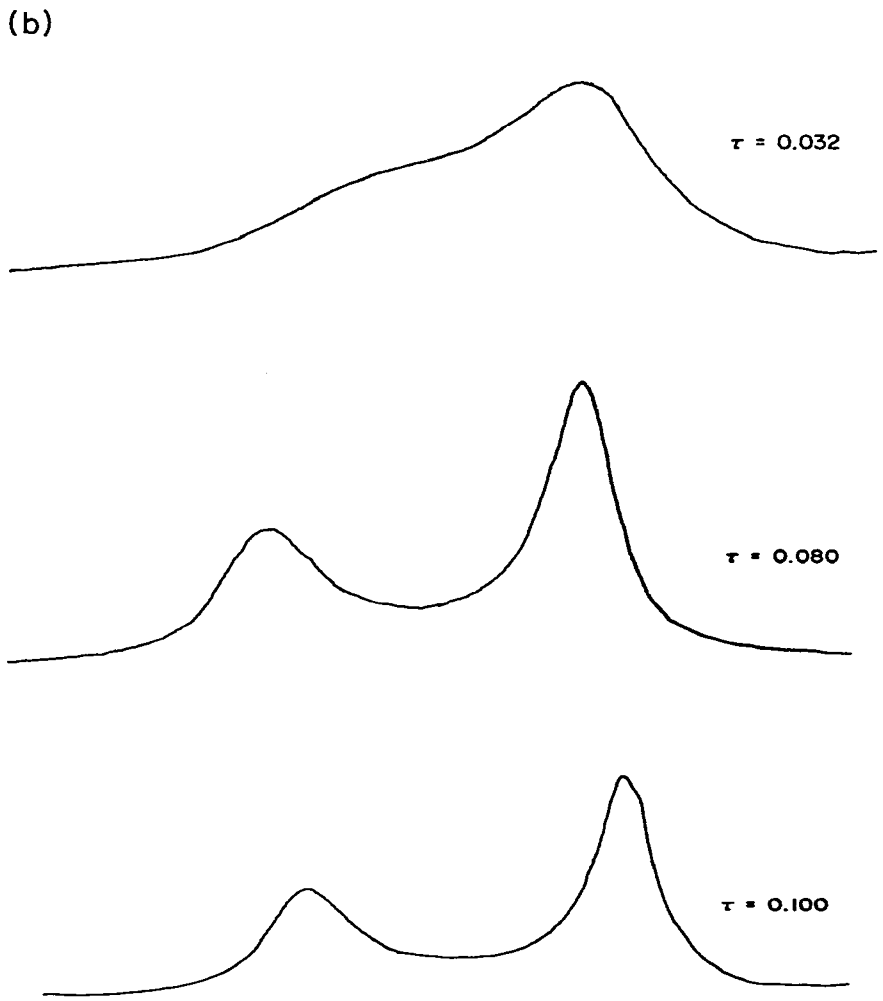


Fig.1. Proton NMR spectra (60 MHz) of I (0.167*M*) and II (0.250*M*) in cyclohexane: (a) experimental spectra as a function of temperature, (b) simulated spectra.

equilibria. The following scheme, which involves a rapid equilibrium followed by a rate-determining step, accounts for both the inverse temperature-rate relation and a β_i value of two which appears to have a significant contribution at all three temperatures studied:

$$2\,\mathrm{Me_3SnBr} \overset{K}{\rightleftarrows} (\mathrm{Me_3SnBr})_2$$

$$\mathrm{Me_3Sn^*I} + (\mathrm{Me_3SnBr})_2 \xrightarrow{k} \mathrm{Me_3Sn^*Br} + \mathrm{Me_3SnBr} + \mathrm{Me_3SnI}$$



The rate expression corresponding to this scheme is

$$\text{Rate} = k\,[\text{I}]\;[(\text{II})_2] = kK\,[\text{I}]\;[\text{II}]^2$$

Since the β value of 2.6 apparently requires the contribution of a term which is at least third order in II, a trimer and even higher aggregates are probably involved in the prior equilibria. Although there is good evidence for molecular association in methyltin halides in the molten state[4], in dilute solution the equilibrium concentrations of these aggregates are likely to be too small to be observed by direct (*e.g.* molecular weight) measurements. The concentration independence of the chemical shifts and $^{117/119}$Sn–C–H coupling constants of I and II in the studied concentration range (0.1–0.5 *M*) are in line with this expectation. This however, does not preclude the existence of small but definite equilibrium concentrations of aggregates which can be all important from the kinetic point of view. As for the inverse temperature-rate relation, the equilibrium concentrations of dimer, trimer and higher aggregates are expected to decrease with increasing temperature and this decrease of K could override the expected increase of k. Thus the decrease of the apparent rate constant with increasing temperature can be rationalized, and in turn it reinforces the evidence for the role of molecular aggregates in this system.

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