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ISOTOPE EFFECTS IN THE BASE CLEAVAGE OF (DIHALOMETHYL)TRIMETHYLTINS. ADDITIONAL EVIDENCE FOR PROPOSED MECHANISTIC PATHWAYS

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Summary

Solvent deuterium isotope effects on the reaction rate (RIE) and on the isotopic composition of the product (PIE) were studied for the three component reactions of the base cleavage of (dihalogenomethyl)trimethyltins ($\text{Me}_3\text{SnCHX}_2$; X = Cl, Br) in 8/2 v/v n-propanol/water in the presence of ammonia buffer. The results support the mechanisms in which free carbanions are separated in the rate determining step in the reactions involving solvent conjugate base, s.c.b., and at the same time confirm the importance of electrophilic assistance of the solvent in the dominant process, which is catalysed by ammonia (general base).

Introduction

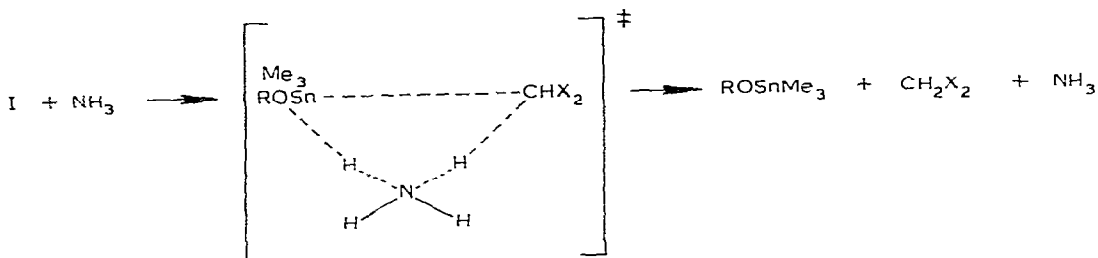
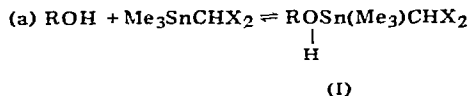
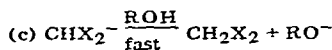
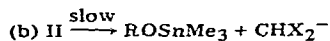
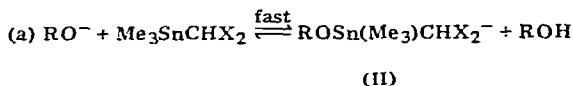
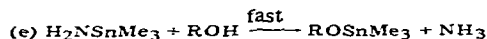
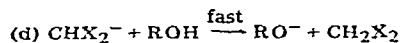
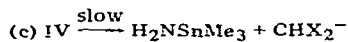
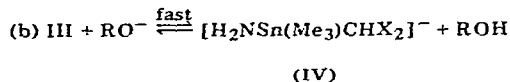
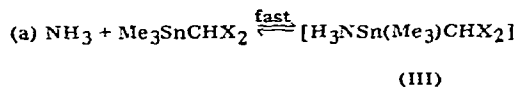
In the previous paper [1] we reported the results of kinetic investigations of solvolysis of $\text{Me}_3\text{SnCHX}_2$ (X = Cl, Br) in basic media. The Sn–C cleavage in n-propanol/water in the presence of ammonia buffer involved three independent catalysed processes: a reaction catalysed by ammonia, acting as general base (k_I), a simple base catalysis (k_{II}) and a base-nucleophilic catalysis (k_{III}) (eqn. 1).

$$-\frac{d[\equiv\text{Sn}-\text{C}\equiv]}{dt} = \{k_I[\text{B}] + k_{II}[\text{OR}^-] + k_{III}[\text{B}][\text{OR}^-]\}[\equiv\text{Sn}-\text{C}\equiv] \quad (1)$$

(R = H, n-Pr; B = weak base (ammonia); OR^- = solvent conjugate base (s.c.b.))

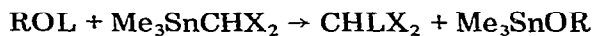
The mechanisms proposed for these processes, shown in Scheme 1, account for the unusual order of reactivity, in which (dihalomethyl)trimethyltins are less readily cleaved than the analogous (dihalomethyl)trimethylsilanes in reactions involving solvent conjugated base.

SCHEME 1

1. General base catalysis by ammonia (k'_1)2. Simple base catalysis (k'_{11})3. Base-nucleophile catalysis (k'_{111})

(X = Cl, Br; R = H, n-Pr)

These mechanistic pathways were suggested, however, only on the basis of the kinetic form and the effect of the leaving group. In order to verify them, we have now determined both the rate (RIE) and product (PIE) solvent isotope effects in deuterated media (PrOD/D₂O, ND₃/ND₄Cl) for all the three component processes. The RIE ($k^{\text{H}}/k^{\text{D}}$) is the overall solvent isotope effect on the reaction rate, while the PIE given by $[\text{CH}_2\text{X}_2]/[\text{CHDX}_2]$ [2] gives information about the detail of the separation of the leaving groups [2].



(L = H, D; R = n-Pr, L)

Results and discussion

The rate constants in the n-PrOD/D₂O, ND₃/ND₄Cl system (k_1^{D} , k_{II}^{D} , $k_{\text{III}}^{\text{D}}$) were determined from equation 2 using the previously described method in a series of experiments at three different buffer ratios [1].

$$\begin{aligned} k_{\text{obs}}^{\text{D}} &= k_1^{\text{D}}[\text{ND}_3] + k_{\text{III}}^{\text{D}}[\text{OR}^-] + k_{\text{III}}^{\text{D}}[\text{ND}_3][\text{OR}^-] \\ &= (k_1^{\text{D}} + k_{\text{III}}^{\text{D}} \frac{[\text{ND}_3]}{[\text{ND}_4\text{Cl}]})[\text{ND}_3] + k_{\text{III}}^{\text{D}} \frac{[\text{ND}_3]}{[\text{ND}_4\text{Cl}]} \end{aligned} \quad (2)$$

The various catalytic constants were calculated, as described previously [1], from the values of the slope and intercept of the linear plot of k_{obs} against the ammonia concentration.

The product isotope effects (PIE's), for simple base catalysis involving s.c.b., were determined in a separate series of runs in a system in which only this particular type of process could occur, namely in 2/1 (H/D) n-propanol/water (8/2 v/v) containing 0.1 M sodium n-propanolate. The overall PIE effect (PIE)_{total} was then determined in the same solvent system containing the ammonia/ammonium chloride catalyst at at least two different buffer concentrations. The (PIE)_{total} is related to the separate PIE's of the component processes as shown in equation 3.

$$(\text{PIE})_{\text{total}} = \alpha_1(\text{PIE})_{\text{I}} + \alpha_2(\text{PIE})_{\text{II}} + \alpha_3(\text{PIE})_{\text{III}} \quad (3)$$

The α 's are factors representing the contribution of the component reactions to the overall process. They are calculated from the known values of the buffer concentrations, the isotopic composition of the medium, the RIE's and the catalytic constants of the component processes. Having measured (PIE)_{total} at two different buffer concentrations we can write a set of two equations, from which values of (PIE)_I for catalysis by general base and (PIE)_{III} for base-nucleophile catalysis may be readily obtained. Usually the values of the PIE's were calculated from more than two different buffer concentrations.

The data relevant to the determination of the isotope effects are summarized in Table 1.

In order to establish whether there was any H/D exchange in the reaction system, which might give rise to inaccurate PIE values for the dihalogenomethanes. CH₂Cl₂ and CH₂Br₂ were kept in the solvolytic media used for the PIE determinations for a period of time corresponding to 100% cleavage of the parent organotin derivatives. In no case was any CHDX₂ or CD₂X₂ (X = Cl, Br) detected, by NMR or mass spectroscopic analysis.

The PIE values for simple base and base-nucleophile catalysis are close to unity in the case of Me₃SnCHCl₂ (1.11 and 1.14, respectively) and exhibit slightly higher values for Me₃SnCHBr₂ (1.30 and 1.28). If the departure from unity were associated with electrophilic assistance by the solvent in the rate

TABLE 1

ISOTOPE EFFECTS IN THE CLEAVAGE OF $\text{Me}_3\text{SnCHX}_2$ ($X = \text{Cl, Br}$) *n*-Propanol/water; ammonia buffer, Temp. 25°C

	$\text{Me}_3\text{SnCHCl}_2$	$\text{Me}_3\text{SnCHBr}_2$
$k_1^{\text{H}} \times 10^8 (\text{l mol}^{-1} \text{s}^{-1})$	41.5 ^a	605 ^a
$k_1^{\text{D}} \times 10^8 (\text{l mol}^{-1} \text{s}^{-1})$	9.0	168
$\text{RIE}(k_1')$	4.6	3.6
$\text{PIE}(k_1')$	1.9	1.7
$\text{RIE}/\text{PIE}(k_1')$	2.4	2.1
$k_{\text{II}}^{\text{H}} \times 10^8 (\text{s}^{-1})$	4.3 ^a	43.7 ^a
$k_{\text{II}}^{\text{D}} \times 10^8 (\text{s}^{-1})$	5.1	48.0
$\text{RIE}(k_{\text{II}}')$	0.84	0.91
$\text{PIE}(k_{\text{II}}')$	1.11	1.30
$\text{RIE}/\text{PIE}(k_{\text{II}}')$	0.76	0.70
$(k_{\text{II}}^{\text{H}}/k_{\text{II}}^{\text{D}})_{\text{sec. (calcd.)}}$	0.73/1.0	0.73/1.0
$k_{\text{III}}^{\text{H}} \times 10^8 (\text{l mol}^{-1} \text{s}^{-1})$	3.0 ^a	51.2 ^a
$k_{\text{III}}^{\text{D}} \times 10^8 (\text{l mol}^{-1} \text{s}^{-1})$	3.26	52.8
$\text{RIE}(k_{\text{III}}')$	0.92	0.97
$\text{PIE}(k_{\text{III}}')$	1.14	1.28
$\text{RIE}/\text{PIE}(k_{\text{III}}')$	0.81	0.76
$(k_{\text{III}}^{\text{H}}/k_{\text{III}}^{\text{D}})_{\text{sec. (calcd.)}}$	0.68/0.96	0.68/0.96

^a Ref. 1.

determining step, that is if steps 2b and 2c were synchronous, and steps 3c and 4d likewise, higher PIE values would be expected for $\text{Me}_3\text{SnCHCl}_2$ then $\text{Me}_3\text{SnCHBr}_2$ since CHCl_2 is a poorer leaving group than CHBr_2 , and so would require more electrophilic assistance. Our findings are contrary to that, which argues in favour of stepwise mechanisms in the processes involving s.c.b., as shown in Scheme 1. In this case the higher PIE's for $\text{Me}_3\text{SnCHBr}_2$ can be associated with the higher stability of the CHBr_2^- carbanion than of CHCl_2^- , which means that CHBr_2^- will be the more selective in the reaction with the protonic solvent.

It must be pointed out that in both reactions involving the participation of solvent conjugated base the values of the ratio RIE/PIE, which can be regarded as a measure of the isotope effect in the nucleophilic attack portion of the substitution process fall in the calculated range for secondary kinetic solvent isotope effects including the equilibrium solvent isotope effect on the s.c.b. concentration (see Experimental) [3]. Thus they are consistent with the absence of proton transfer in the rate determining step, supporting the proposed stepwise mechanisms for simple base and base-nucleophilic catalysis.

Much higher values of product isotope effect were found for the general base catalysed reaction, which is consistent with a different type of mechanism, involving proton transfer synchronous with the Sn—C bond cleavage.

The PIE value is slightly higher for $\text{Me}_3\text{SnCHCl}_2$ (1.90) than for $\text{Me}_3\text{SnCHBr}_2$ (1.70). This corresponds well with the expected, more advanced extent of

Sn—C bond breaking in the transition state in the case of $\text{Me}_3\text{SnCHCl}_2$, which would be expected from the respective leaving group abilities ($\text{CHCl}_2 < \text{CHBr}_2$), with the degree of C—H bond formation in the transition state less than 0.5 [4].

The high values of the ratio $(\text{RIE})/(\text{PIE})$ for the catalysis by ammonia as general base, e.g. 2.4 and 2.1 for the CHCl_2 and CHBr_2 derivatives, respectively, confirm that the proton transfer associated with the nucleophilic attack at tin (e.g. from the R—OSn to the base) also occurs in the rate determining step,



which is as required for the general base catalysed process.

The determination of isotope effects has provided new evidence in support of the mechanisms proposed for the processes leading to Sn—C bond cleavage in the presence of ammonia buffer [1]. Electrophilic assistance, proved for the reaction involving general base catalysis, shows the importance of previously postulated additional pulling force, which facilitates Sn—C bond heterolysis [5,6]. It also indicates that lack of such electrophilic assistance must be responsible for the lower reactivity of $\text{Me}_3\text{SnCHX}_2$ than their silicon analogues [1,7] in the s.c.b. catalysed cleavages. The observations are in accordance with the suggestion by Eaborn et al. [5,6,8] that Sn—C bonds are cleaved more readily than Si—C bonds when assisted by electrophiles, while the opposite sequence is observed when the cleavage leads to generation of the carbanion. So, the reactions with s.c.b, involving stepwise processes, are presumably less favourable pathways compared to the synchronous process observed in general base catalysis.

Experimental

General

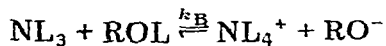
The preparations of the compounds, the compositions of the media, and the methods used for rate measurements have been described previously [1,9–13].

PIE measurements

These were carried out in a solvent system having an available H/D ratio of 2/1. After the cleavage was complete, as checked by GLC analyses, the product ratio $\text{CH}_2\text{X}_2/\text{CHDX}_2$ was determined by two independent methods (^1H NMR and GC-MS) for at least three separate runs at each given buffer composition or NaOR concentration. The results were reproducible and the same PIE values were obtained by both methods. The mass spectroscopy analyses were found to give a lower standard deviation (0.03) and were used for PIE calculations. The PIE value is given by halving the observed product ratio $\text{CH}_2\text{X}_2/\text{CHDX}_2$.

Estimation of the secondary kinetic isotope effect ($k^{\text{H}}/k^{\text{D}}$)_{sec}.

The $(k^{\text{H}}/k^{\text{D}})_{\text{sec}}$ was calculated for both reactions with s.c.b. participation using an approximate analysis based on fractionation factors given by Schowen [3]. First, the contribution due to the equilibrium isotope effect on the s.c.b. concentration was calculated.



$$\frac{K_B^H}{K_B^D} = \frac{\rho_{OL}^2 \rho_{NL}^3}{\rho_{NL}^4 + \rho_{RO}^-} = \frac{(1.0)^2 (0.92)^3}{(0.97)^4 (0.47 - 0.56)} = 1.56 - 1.86$$

Then the secondary kinetic isotope effect in the transition state, $(k^H/k^D)_{\text{sec.}}$, was calculated assuming that the bond making between the nucleophile and the tin atom is complete in the transition state as required in the stepwise mechanism*. For example, for simple catalysis.

$$\left(\frac{k_{II}^H}{k_{II}^D}\right)_{\text{sec.}} = \frac{\rho_{OL^-}}{\rho_{OL}} = \frac{0.47 - 0.56}{1} = 0.47 - 0.56$$

The net secondary kinetic solvent isotope effect was calculated as the product of these two contributing effects

$$\left(\frac{k_{II}^{\prime H}}{k_{II}^{\prime D}}\right)_{\text{sec.}} = \frac{K_B^H}{K_B^D} \left(\frac{k_{II}^H}{k_{II}^D}\right)_{\text{sec.}} = 0.73 - 1.0.$$

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* The proton transfer from ammonia to the s.c.b. in the base-nucleophile catalysed process was also assumed to be complete in the transition state.