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CATALYTIC REACTIONS IN Sn—C BOND CLEAVAGE IN BASIC MEDIA

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Summary

Kinetics of solvolysis of (dihalomethyl)trimethyltins (Me_3SnCHX_2; X = Cl, Br) have been studied in the solvent system n-propanol-water 8 : 2 v/v, using ammonia buffer. In addition to simple base catalysis involving Sn—C bond cleavage by solvent conjugate base, the reaction shows catalysis by ammonia acting as a general base as well as base nucleophile catalysis with participation of both ammonia and solvent conjugate base. Comparison of the catalytic constants for these three types of catalysis with those for the Me_3SiCHX_2 series reveals the enhanced role of general base catalysis in the cleavage of the tin compounds. Both of the reactions involving solvent conjugate base were slower for the tin compounds than for the silicon analogues.

Introduction

Our earlier studies revealed that several types of catalysis are involved in silicon—carbon bond cleavage in basic media [1]. We have now extended our investigations to the analogous dihalomethyl derivatives of tin Me_3SnCHX_2; X = Cl, Br in order to establish the scope of such catalysis for nucleophilic cleavage of various M—C bonds (where M refers to a Group IV element). It is also of interest to examine the influence of the change in size, polarizability and bond polarity of the central atom on mechanistic pathways for nucleophilic displacement in Group IV, a problem which is being studied by Eaborn and coworkers [2,3].

Results and discussion

Our investigation centred on the kinetic study of the solvolytic cleavage of the Sn—C bond. This was carried out in 8 : 2 v/v n-propanol-water solution in the presence of ammonia buffer, with lithium chloride present to maintain constant ionic strength.

TABLE 1

KINETIC RESULTS FOR (Me_3SnCHX_2) [a]

X	[Me_3SnCHX_2]	[NH_3] (M)	[NH_4Cl] (M)	[NH_3]/[NH_4Cl]	$k_{obs.} \times 10^6$ (s^{-1})
Br	0.10	0.20	0.037	5.41	3.90
	0.60	0.20	0.037	5.41	3.85
	0.30	0.20	0.037	5.41	3.88
	0.30	1.0	0.185	5.41	11.48
	0.30	1.266	0.234	5.41	13.55
	0.30	2.0	0.370	5.41	19.83
	0.30	0.20	0.017	11.82	7.92
	0.30	0.46	0.039	11.82	10.00
	0.30	1.38	0.117	11.82	23.00
	0.30	2.30	0.195	11.82	32.67
	0.30	0.193	0.007	28.00	16.33
	0.30	0.483	0.017	28.00	21.00
	0.30	1.410	0.050	28.00	41.67
	0.30	2.80	0.1	28.00	70.00
Cl	0.25	0.1998	0.0027	74	3.68
	0.25	0.74	0.01	74	4.93
	0.25	1.976	0.0267	74	8.80
	0.25	2.96	0.04	74	10.95
	0.25	0.1937	0.0013	149	7.33
	0.25	0.745	0.005	149	10.00
	0.25	1.9817	0.0133	149	15.48
	0.25	2.98	0.02	149	20.80
	0.25	0.203	0.0007	290	14.67
	0.25	0.725	0.0025	290	19.67
	0.25	1.943	0.0067	290	31.17
	0.25	2.9	0.01	290	40.50

[a] n-PrOH - H_2O system 8 : 2 v/v, $\mu = 0.4$, $t = 25°C$.

The cleavage was monitored by GLC determination of the CH_2Cl_2 and CH_2Br_2 formed as the reaction progressed. This revealed that the reactions were of first order with respect to (dihalomethyl)trimethyltin. The observed first order rate constants are given in Table 1. Three independent series of runs at different buffer ratio were performed for the (dihalomethyl)trimethyltins. This approach enabled us to distinguish clearly between the three types of catalytic reactions represented in the following rate equation:

$$\frac{-d[Sn{-}C]}{dt} = \{k_I[B] + k_{II}[OR^-] + k_{III}[B][OR^-]\}[substrate]$$

R = H, n-Pr

where k_I corresponds to the rate constant for catalysis by weak base, k_{II} for simple catalysis with s.c.b. (solvent conjugate base) participation, and k_{III} for base - nucleophile catalysis involving weak base and solvent conjugate base (s.c.b.) *.

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* This process involves the base catalysed ammonolysis of the Sn—C bond, followed by the fast hydrolysis of the unstable product Me_3SnNH_2.

The processes represented by k_{II} and k_{III} were found previously for (dihaloalkyl)trimethylsilanes [4], while the remaining catalytic reaction was distinctly observed with the more reactive (trihalomethyl)trimethylsilanes and 1-dibromomethyl-1-methylsilacyclobutane [5]. The kinetic analysis of the data for Me_3SnCHX_2, illustrated by Fig. 1, gave the values of the respective catalytic constants: k'_I for general base catalysis, k'_{II} for simple catalysis, and k'_{III} for base-nucleophile catalysis.

$$
\begin{aligned}
k_{obs} &= k_I[NH_3] + k_{II}[OR^-] + k_{III}[NH_3][OR^-] \\
&= \left\{k'_I + k'_{III}\frac{[NH_3]}{[NH_4Cl]}\right\}[NH_3] + k'_{II}\frac{[NH_3]}{[NH_4Cl]}
\end{aligned}
$$

The mechanisms of component catalytic reactions must be close to those established for the dihaloalkylsilanes. We should point out, however, that the

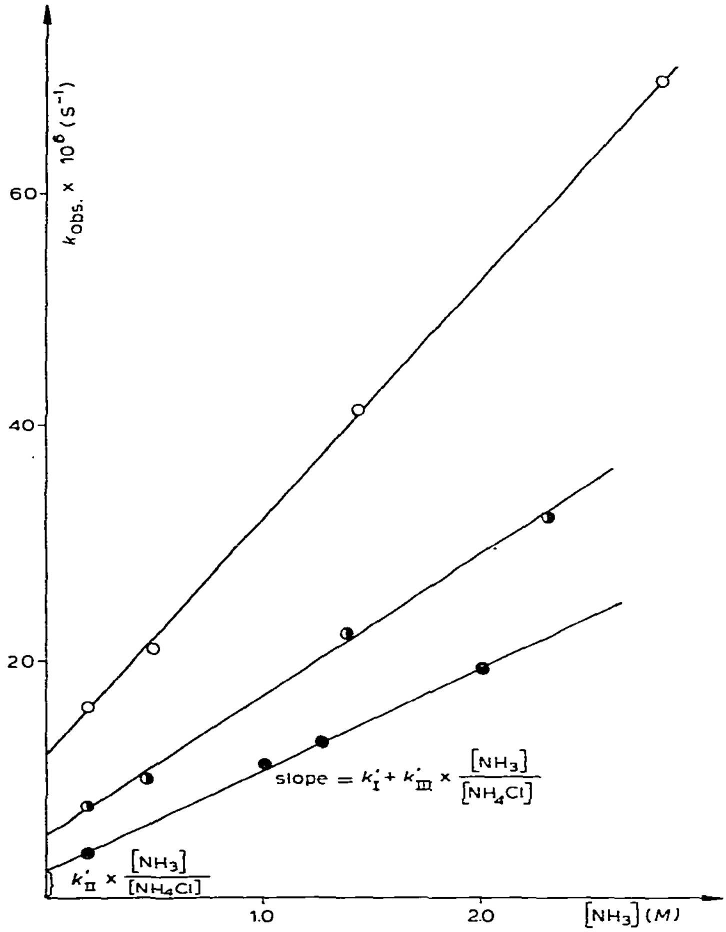


Fig. 1. Dependence of the observed first order rate constant on the ammonia concentration for the cleavage of $Me_3Sn(CHBr_2)$ in PrOH-H_2O 8 : 2 v/v at 25°C at three different buffer ratio values. $[NH_3]/[NH_4Cl]$: ○, 29; ◑, 11.8; ●, 5.4.

stepwise mechanisms seem to be more probable for organotin derivatives [6], i.e. those involving formation of Sn^V intermediates $[ROSn(Me_3)CHX_2]$ and $[H_2NSn(Me_3)CHX_2]^-$ in the simple base and base-nucleophile catalyses (Scheme 1). The route involving proton transfer from the leaving group CHX_2 to the

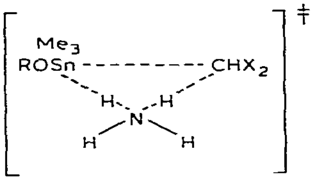
SCHEME 1

1. General base catalysis by ammonia (k'_I)

(a) $ROH + Me_3SnCHX_2 \rightleftharpoons [\underset{H}{RO}Sn(Me_3)CHX_2]$

(I)

(b) $I + NH_3 \longrightarrow$



$\longrightarrow ROSnMe_3 + CH_2X_2 + NH_3$

2. Simple base catalysis (k'_{II})

(a) $RO^- + Me_3SnCHX_2 \rightleftharpoons [ROSn(Me_3)CHX_2]^-$

(II)

(b) $II \xrightarrow{slow} ROSnMe_3 + CHX_2^-$

3. Base-nucleophile catalysis (k'_{III})

(a) $NH_3 + Me_3SnCHX_2 \rightleftharpoons [H_3NSn(Me_3)CHX_2]$

(III)

(b) $III + RO^- \rightleftharpoons [H_2NSn(Me_3)CHX_2]^-$

(IV)

(c) $IV \xrightarrow{slow} H_2NSnMe_3 + CHX_2^-$

$\xrightarrow{ROH}$

$ROSnMe_3 + CH_2X_2$

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

base, e.g.:

$$[H_3NSn(Me_3)CHX_2] \underset{ROH}{\overset{^-OR}{\rightleftharpoons}} [H_3NSn(Me_3)CX_2]^-$$

may be excluded since solvolysis in deuterated media led to quantitative formation of $CHDX_2$ [7].

In the reaction involving general catalysis, Sn—C bond breaking is synchronous with proton transfer (1b). The possibility of direct nucleophilic attack of ammonia on the tin atom seems remote, since it should be more important for silicon than tin derivatives and was not detected for (dihalomethyl)silanes (Table 2).

The rate determining step in all cases is cleavage of the Sn—C bond as demon-

TABLE 2

RATE CONSTANTS FOR THE SOLVOLYSIS OF Me_3MCHX_2 (M = Si, Sn; X = Cl, Br)

	$Me_3SiCHCl_2$ [a]	$Me_3SnCHCl_2$ [b]	$Me_3SiCHBr_2$ [a]	$Me_3SnCHBr_2$ [b]
$k'_I \times 10^8$ [$l\ mol^{-1}\ s^{-1}$]	<1.0 [c]	41.5	<10 [c]	605
$k'_{II} \times 10^8$ [s^{-1}]	9.2	4.3	1050	43.7
$k'_{III} \times 10^8$ [$l\ mol^{-1}\ s^{-1}$]	69.9	3.0	1690	51.2

[a] Ref. 4. [b] This work. [c] Undetected [4], must be less than the values given.

strated by the higher specific rate constants for $Me_3SnCHBr_2$ than for $Me_3SnCHCl_2$, in accord with the order of CHX_2^- anion stability [8]. The important contribution by the catalysis involving the weak base ammonia is a striking feature of the $\equiv$Sn—CHX_2 bond cleavage. In the case of analogous $\equiv$Si—CHX_2 cleavage this type of catalysis is strongly overwhelmed by the reactions involving s.c.b. Presumably the greater softness of Sn compared with Si is responsible for this behaviour. Soft carbanions should show a higher "philicity" towards tin [6] than do OR^- and NH_2^-. Thus, Sn^V intermediates II and IV should decompose much more readily to the substrates than to the products when compared with the analogous Si^V intermediates. This factor should be less important in general catalysis, and so therefore the catalysis can be more effective in Sn—C bond cleavage. This conclusion is supported by the greater enhancement of general base catalysis in cleavage of $Me_3SnCHBr_2$ compared with that of $Me_3SnCHCl_2$.

Another interesting feature of the data in Table 2 is the lower reactivity in the processes involving s.c.b. for the organotin compounds than for their organosilicon analogues. The Sn—C bonds in aryl and benzyl derivatives of tin are known to be more readily cleaved by NaOMe/MeOH than the corresponding Si—C bonds [2,3] although the opposite order has been observed in some media [15]. The unusual reactivity order observed in our systems may be a feature of the solvent system we used (a medium of lower basicity) or may reflect our use of better leaving groups.

It could be argued that the unusual order in reactivity is due to an interaction between the halogen and tin atoms which stabilizes the initial state. Any intermolecular association (such as that postulated by Mitchell [9]) cannot be important in our solvolytic system since molecular weight measurements in n-propanol gave only slightly higher values than expected for monomeric species: 310 (calcd. 248) and 400 (calcd. 337) for $Me_3SnCHCl_2$ and $Me_3SnCHBr_2$, respectively. As for intramolecular interaction, $(p\text{—}d)\sigma$ conjugation and the so called α-effect [10] must be taken into account. The Mössbauer spectrum of $Me_3SnCHBr_2$ shows a chemical shift of δ 1.33 mm s^{-1} and a distinct quadrupole splitting of $\Delta = 1.24$ mm s^{-1} which can be interpreted in terms of participation of an unshared electron pair of a halogen in bonding with the tin [11].

Experimental

General

All solvents and reactants were carefully dried by standard techniques.

The method used for the rate measurements was described previously [4,12], as were the conditions for GLC analysis. A 302B Hewlett Packard Vapor Pressure Osmometer was used for molecular weights measurements.

(Dihalomethyl)trimethyltins

(Dichloromethyl)trimethyltin was prepared from $LiCHCl_2$ and Me_3SnCl in THF/Et_2O/pentane [13]. (Dibromomethyl)trimethyltin was made by a low temperature Grignard reaction between dibromomethylmagnesium bromide and Me_3SnCl [14]. Organotin compounds were carefully fractionated through a spinning band column and kept under nitrogen.

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