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BASE CLEAVAGE OF SOME BENZYL–SILICON AND TIN COMPOUNDS IN H_2O – MeOH – CYCLODEXTRIN MEDIUM

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الملخص

لقد تمت دراسة تأثير ألفا ـ وبيتا ـ سيكلوديكترينز على معدل سرعة التفاعل بواسطة قاعدة على $3,5-Cl_2.C_6H_3CH_2.MMe_3$, $4-ClC_6H_4CH_2MMe_3$. $3-ClC_6H_4CH_2MMe_3$ حيث ان $M = Si, Sn$. ألفا ـ وبيتا ـ سيكلوديكترينز تزيد من معدل سرعة التفاعل في حالة مركبات القصدير $RSnMe_3$ ولكن لا يوجد اي حفز ذو مغزى في حالة مركبات السيليكون المشابهة $RSiMe_3$

ABSTRACT

The effects of ∝ – and ß– cyclodextrin (∝ – , ß– CD's) on the rates of base cleavage of $4-CNC_6H_4SnMe_3$,$3-ClC_6H_4CH_2MMe_3$, $4-ClC_6H_4CH_2-MMe_3$, and $3,5-CL_2C_6H_3CH_2MMe_3$ with M = Si and Sn have been examined in H_2O – MeOH medium . ∝ – and ß–CD's accelerate the cleavage of the $RSnMe_3$ compounds (R=3-$ClC_6H_4CH_2$, 4–$ClC_6H_4CH_2$, and 3,5 – $Cl_2C_6H_3CH_2$) . There is no significant catalysis in the case of the corresponding silicon compounds .

INTRODUCTION

Extensive studies have been made of base cleavage of R-MMe_3 bonds , where M = Si or Sn and R is an organic group , usually of the aryl or benzyl type [1-9] . The medium of NaOMe-MeOH has been most frequently used , and in it the cleavages of the silicon and tin compounds have been shown to differ in mechanism ; for the silicon compounds the rate determining step involves the separation of the carbanion R^- mechanism B (or B_s) , whereas for most tin compounds the breaking of the Sn – R bond is accompanied by proton transfer (electrophilic assistance) from the solvent to the separating carbon center [5-8] mechanism A (or A_s) . The exceptions for tin compounds arise in the case of very reactive species , for example with R = 9–fluorenyl , which appear to undego cleavage without electrophilic assistance [8] mechanism B (or B_s) .

The following mechanisms were suggested[7,11,12,13] for cleavage of some benzyltrimethylsilanes and stannanes by methanolic sodium methoxide :

1) A .

$$MeO^- + Me_3MR \rightleftharpoons [MeOMMe_3R]^- .$$

$$[MeOMMe_3R]^- + MeOH \longrightarrow [MeO-MMe_3 ....R....H....OMe]^- \longrightarrow$$

Transition State

$$MeOMMe_3 + RH + MeO^- .$$

2) A_s .

$$MeO^- + Me_3MR + MeOH \longrightarrow [MeO-MMe_3 ....R....H....OMe]^- \longrightarrow$$

Transition State

$$MeOMMe_3 + RH + MeO^- .$$

3) B.

$$MeO^- + Me_3MR \rightleftharpoons [MeOMMe_3R]^-.$$

$$[MeOMMe_3R]^- \longrightarrow [MeO-MMe_3 \ldots R]^- \longrightarrow MeOMMe_3 + R^-.$$

Transition State

$$R^- + MeOH \longrightarrow RH + MeO^- (fast)$$

4) B_s.

$$MeO^- + Me_3MR \longrightarrow [MeO-MMe_3 \ldots R]^- \longrightarrow MeOMMe_3 + R^-.$$

Transition State

$$R^- + MeOH \longrightarrow RH + MeO^- (fast)$$

For cleavage of Benzylsilicon compounds , in a medium of fairly high water content (36 vol %) , the value of the specific rate constant , k_s , given by the observed first-order rate constant divided by the base concentration , is fairly constant over a wide range of base concentration Where as in methanol depends markedly on the sodium methoxide concentration [10].

EXPERIMENTAL

Preparation of organosilicon and organotin compunds

The $XC_6H_4CH_2SiMe_3$ compounds were made by standard methods, viz.(X =) , 3-Cl[23], 4-Cl [24] . $4-ClC_6H_4CH_2SnMe_3$ was made by the standard method[24]

The following compunds were kindly supplied by Professor C.Eaborn : ($3,5-Cl_2C_6H_3CH_2SiMe_3$) $3,5-Cl_2C_6H_3CH_2SnMe_3$, $3-ClC_6H_4CH_2SnMe_3$ $4-CNC_6H_4CH_2SnMe_3$.

Rate measurments

The rates of the cleavage of organosilicon , and organotin compounds were measured spectrophotometrically using a Unicam SP 1700 with automatic recording system . The machine was fitted with a thermostatically controlled cell-holder accurate to within ± 0.1° .

Cyclodextrin solutions were prepared as folows . The CD was dissolved in water (5 ml) and (4 ml) sample of the sodium methoxide solution in methanol was then added . A (4 ml) sample of the resulting solution was added to (1 ml) of the solution of the organometallic in methanol . The mixture was shaken and transferred to the stoppered quartz cell (10 mm path length) and the change in UV absorption at the selected wavelength was recorded . The reference cell was filled with aqueous methanol .

optical density readings were recorded at convenient intervals up to three half-lives . The **infinity** readings were taken after ten half-lives. The spectra were found to be in good agreement with solutions of authentic samples of the appropriate toluene at the correct concentration in the cleavage medium .

The following wavelengths were used in the rate studies :
3,5 – Cl_2 – C_6H_3 CH_2 $SnMe_3$, 280 ; 3,5 – Cl_2 C_6H_3 $SiMe_3$, 283.5 ;

3 – ClC_6 H_4CH_2 $SnMe_3$, 286 ; 3 – ClC_6H_4 CH_2 $SiMe_3$, 279.5 ;

4 – ClC_6 $H_4CH_2SnMe_3$, 286 ; 4 – $ClC_6H_4CH_2SiMe_3$, 278 ; 4 – $CNC_6H_4CH_2$ $SnMe_3$, 270 nm .

RESULTS

We have now examined the cleavages of 3,5 - $Cl_2C_6H_3MMe_3$, 3 – Cl- $C_6H_4CH_2MMe_3$, 4 – $ClC_6H_4CH_2MMe_3$, and 4 – $CNC_6H_4CH_2SnMe_3$ catalysed by α - and β –CD and the results are shown in Tables 1 and 2 .

Table 1

Rates of cleavage of $RMMe_3$ by $NaOH–H_2O–MeOH–\alpha$ – CD at 50°

R	10^3[α–CD]/M	H_2O:MeOH by volume	[NaOH]★/M	$RSnMe_3$ 10^5ks/l $mol^{-1}s^{-1}$	$RSiMe_3$ 10^5ks/l $mol^{-1}s^{-1}$
$3,5–Cl_2C_6H_3CH_2$	0	44:56	0.238	913.33	109.50
	41.79	44:56	0.238	2206.33	127.73
	26.82	44:56	0.031	4386.67	—
	0	44:56	0.031	1155.17	—
$3–ClC_6H_4CH_2$	0	44:56	0.953	26.72	2.72
	41.79	44:56	0.953	75.77	2.35
$4–ClC_6H_4CH_2$	0	44:56	0.953	8.33	0.43
	41.79	44:56	0.953	20.20	0.48

★ The base is denoted throughout by NaOH although both hydroxide and methoxideions are present .

Table 2

Rates of cleavage of $RMMe_3$. by $NaOH–H_2O–MeOH–ß–CD$ at 50°.

R	10^3.[ß–CD]/M	H_2O:MeOH by volume	[NaOH]/M	$RSnMe_3$. 10^5ks/ l $mol^{-1}s^{-1}$.	$RSiMe_3$. 10^5ks/ l $mol^{-1}s^{-1}$.
$3,5–Cl_2C_6H_3CH_2$.	3.69	23.8:76.2	0.306	1794.0	118.65
	38.50	44:56	0.238	2116.5	84.93
	58.03	44:56	0.257	2197.2	96.67
	22.03	44:56	0.031	5333.3	---
	13.66	44:56	0.052	3219.7	---
	22.03	44:56	0.100	2888.2	---
	15.86	44:56	0.205	2336.5	---
	44.05	44:56	0.482	1997.3	---
	0	44:56	0.031	1155.2	---
	0	44:56	0.10(	837.0	---
	0	44:56	0.205	983.8	---
$3–ClC_6H_4CH_2$.	0	44:56	0.953	26.72	2.72
	28.4	37.5:62.5	1.089	61.67	2.98
	39.5	44:56	0.953	80.00	2.07
	44.05	44:56	0.483	59.50	---
$4–CNC_6H_4CH_2$.	0	0:100	0.007 *	66666.7	---
	7.36	44:56	0.007	64116.7	---

* The base is NaOMe.

It is seen from Table 1 that ∝ -CD catalyses the cleavage of 3,5– $Cl_2C_6H_3CH_2$ – $SnMe_3$, 3–Cl $C_6H_4CH_2SnMe_3$, and 4–Cl $C_6H_4CH_2SnMe_3$ by a factor of Ca . 2.5 at a moderate base concentration and by the larger factor of Ca . 3.8 at a lower base concentration [0.03 M] . For the corresponding silicon compounds there is a little or no acceleration by ∝ – CD .

In Table 2 results are listed for the addition of ß–CD to the cleaving medium , and it will be seen that the effects are very similar .

The lower rates for cleavage of some organosilicon compounds in the presence rather than in the absence of ß–CD as shown in Table 2 .

For the cleavage of 4–$CNC_6H_4CH_2SnMe_3$ there is no catalysis by ß–CD as shown in Table 2 .

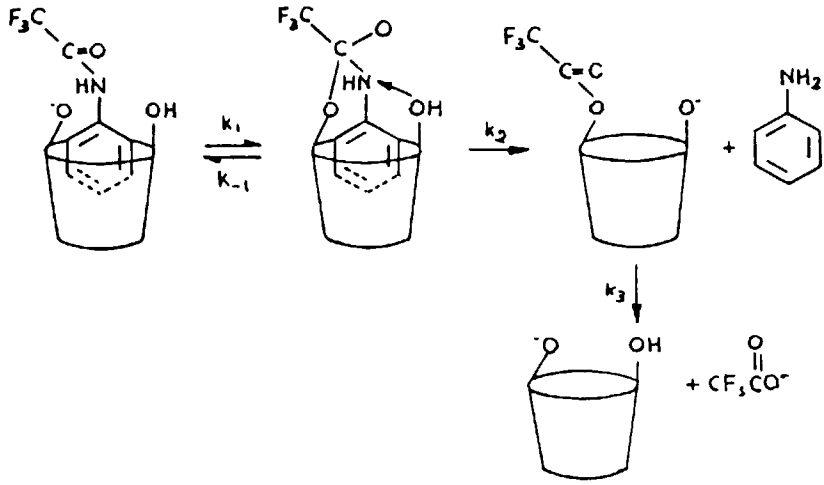
There has been no change in the ultraviolet spectrum of 3–Cl $C_6H_4CH_2MMe_3$ or 3,5–$Cl_2C_6H_3CH_2MMe_3$ when ∝ – or ß–CD was added .

DISCUSSION

Cyclodextrins are fairly stable in alkaline solution , but are rather susceptible to acid catalysis [14] .

Both ∝ – and ß –CD's accelerate the cleavage of a variety of phenyl esters . The catalysis by CD's varies widely , from 300 fold for m–nitrophenyl acetate to 1.1 fold for t–butylphenyl acetate [15] .

The ∝ – CD catalysed hydrolsyis of p-nitrofluoroacetanilide is thought to involve the process shown below[16]



As shown in Tables 1 and 2 there is a difference in the behaviour of tin and silicon compounds . Catalysis by both ∝ and ß – CD's is covalent which was observed in the cleavage of phenyl acetates and acetanilides [15] . In this catalysis the secondary hydroxyl group (in the ionic stage) will provide the nucleophile to attack the metal atom in the compounds shown in Tables 1 and 2 . Evidence for the extensive ionization of the secondary hydroxyl groups (pka 12) [17- 19] is provided by the observation that during the preperation of the cleavage systems , the solubility of both ∝ and ß – CD's in aqueous methanol was increased by addition of base (NaOMe).

The higher catalysis by ∝ - and ß - CD's catalysed cleavages of the organotin compound ($3,5\text{-}Cl_2C_6H_3CH_2SnMe_3$) at low base concentration is in support of electrophilic assistance by the unionized secondary hydroxyl groups which are more available at low than at higher base concentration .

The lower rates of some organsilicon compounds in the presence rather than in the absence of ß–CD are possibly due to the fact that some NaOMe will be used in the ionization of secondary hydroxyl groups of ß–CD and the resulting anions will be very poor nucleophiles .

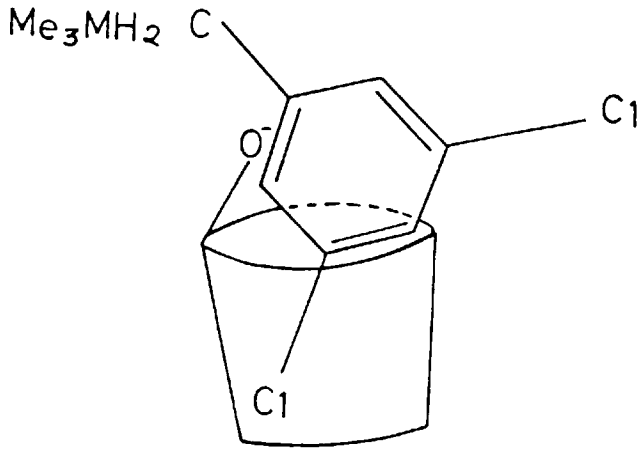
The above results are consistent with the electrophilic assistance by solvent (in CD's it is by the unioised secondary hydroxyl groups) in the rate-determining step in the cleavage of $RSnMe_3$ compounds

R = $3,5\text{–}Cl_2C_6H_3CH_2$, $3\text{–}ClC_6H_4CH_2$, and $4\text{–}ClC_6H_6H_4CH_2$.

For the cleavage of $4\text{-}CNC_6H_4CH_2SnMe_3$ there is no catalysis by ß–CD as shown in Table 2 . This suggests that this compound possibly reacts by the ionization mechanism B (or Bs) , that is the mechanism which operates for the cleavage of benzylsilicon compounds , and it is significant that Eaborn et al [8] suggested that the mechanistic crossover point for cleavages of $XC_6H_4CH_2SnMe_3$ compunds in MeOH-MeONa lies near the compound with X = 4 – CN.

The possibility was considered that it might be the $SnMe_3$ group and not the aryl group which enters the cavity of the CD , but a simple calculation indicated that the diameter of this group (viz . 7.55 A°) was markedly greater than that of the cavity (viz.7 A°) [20] . However calculation also indicated that the width of the $3,5 – Cl_2C_6H_3CH_2$ position of the $3,5 – Cl_2C_6H_3CH_2MMe_3$. (viz.9.12 A°)

is also too great to permit full entry into the cavity ; however this would also be the case for the 3,5 – $Me_2C_6H_3$ – group , and yet both ∝ – and ß – CD's are shown to catalyse the reactions of dimethylphenyl acetates [21] . It is conceivable that only part of the 3,5 - $CL_2C_6H_3$ – group enters the cavity , as shown below .



It is relevant in this connection to note that in hydrolysis of phenyl esters , meta – substituted phenyl esters show larger acceleration by CD than corresponding para – compound , and meta / para specifity is larger for esters with more bulky substituents . These are due to the geometry of the inclusion complexes , especially the distance between the electrophilic centers (the carbon atom in phenyl esters) and the nucleophilic catalytic center (a secondary hydroxyl group of the CD) .[22]

Finally we note that we obtained no change in the ultraviolet spectrum of 3 – $ClC_6H_4CH_2MMe_3$ or 3,5 – $Cl_2C_6H_3CH_2MMe_3$ when ∝ – or ß – CD was added . This indicates that there is only a small degree of inclusion even in the case of the tin compounds , which is perhaps not surprising since the organic group will have a substantially greater affinity for these methanolic media than for the aqueous media usually used with CD'S , and so shows a lower tendency to enter the non–polar cavity . Since the degree of inclusion is so small , in our media , this implies that the reactivity of an included molecule must be exceptionally high to give rise to the marked catalysis observed .

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