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THE MEDIUM DEPENDENCE OF THE RATES OF BASE CLEAVAGE OF CARBON—SILICON AND —TIN BONDS

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Summary

Rates of cleavage of Me_3MR compounds ($M = Si$, $R = m\text{-}ClC_6H_4CH_2$, $p\text{-}NO_2C_6H_4CH_2$, Ph_2CH, 9-fluorenyl, and 2-benzothienyl; $M = Sn$, $R = m\text{-}ClC_6H_4CH_2$, Ph_2CH, 2-benzothienyl) have been measured in $Me_2SO/MeOH/MeONa$, $Me_2SO/EtOH/EtONa$, and $Me_2SO/H_2O/HONMe_4$ media containing varying amounts of the hydroxylic component. The variations in the slopes of the log k_{rel} — H_- plots are consistent with the view that a water or alcohol molecule provides electrophilic assistance in the rate-determining step for the tin compounds with $R = m\text{-}ClC_6H_4CH_2$ and 2-benzothienyl, while for the silicon compounds, and possibly for the tin compound with $R = Ph_2CH$, carbanions are liberated in the rate-determining step.

Introduction

Recent studies of the base-catalysed cleavage of Me_3M—R bonds with M = Si or Sn have revealed mechanistically significant differences in behaviour between the silicon and tin compounds. In particular, the solvent isotope effects for cleavage by sodium methoxide in methanol indicate that for Me_3SnR compounds with $R = XC_6H_4CH_2$, XC_6H_4, or a heterocyclic aryl group, viz. 2-C_4H_3O (2-furyl), 2-C_4H_3S (2-thienyl), 2-C_8H_5O (2-benzofuryl), and 2-C_8H_5S (2-benzothienyl), the breaking of the Sn—R bond occurs in the rate-determining step and is electro-

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philically assisted by proton transfer from the solvent, probably in a mechanism (see Scheme 1) of type A (or possibly A_s) [1—3]. For silicon compounds, on the

SCHEME 1. Mechanisms of base cleavage of $Me_3M—R$ bonds by methanolic sodium methoxide

(1) Type A:

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

$$[MeOMMe_3R]^- + MeOH \rightarrow \underset{\text{transition state}}{[MeO—MMe_3 \text{---} R \text{----} H \text{--} OMe]^-} \rightarrow MeOMMe_3 + RH + MeO^-$$

(2) Type A_S:

$$MeO^- + Me_3MR + MeOH \rightarrow \underset{\text{transition state}}{[MeO\text{—-}MMe_3 \text{---} R \text{----} H \text{--} OMe]} \rightarrow MeOMMe_3 + RH + MeO^-$$

(3) Type B:

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

$$[MeOMMe_3R]^- \rightarrow \underset{\text{transition state}}{[MeO — MMe_3 \text{---} R]^-} \rightarrow MeOMMe_3 + R^-$$

$$R^- + MeOH \rightarrow RH + MeO^- \qquad \text{(fast)}$$

(4) Type B_S:

$$MeO^- + Me_3MR \rightarrow \underset{\text{transition state}}{[MeO\text{—-}MMe_3 \text{---} R]^-} \rightarrow MeOMMe_3 + R^-$$

$$R^- + MeOH \rightarrow RH + MeO^- \qquad \text{(fast)}$$

other hand, with R = $XC_6H_4CH_2$, 2-C_4H_3O, 2-C_4H_3S, 2-C_8H_5O, and 2-C_8H_5S, such electrophilic assistance appears to be absent, or at least undetectably small [3]. It can be ruled out with confidence for highly reactive compounds such as those with R = 2-fluorenyl, 1-indenyl, or *p*-nitrobenzyl, the process then involving rate-determining carbanion separation, as in mechanism B (or, less likely, B_s), and since there appears to be no discontinuity in behaviour between these compounds and that with R = Ph_3C, Ph_2CH_2, $PhCH_2$, and other less reactive XC_6H_4-CH_2 compounds [4], it is likely that free carbanions R^- are also generated in these cases in the rate-determining step [3]. If these conclusions are correct, a methanol molecule is involved (as a reagent) in the rate-determining transition state for the tin compounds but not for the silicon compounds *, and this should be reflected in different dependence on medium composition [6]. We describe below experiments which demonstrate such a difference.

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* For simplicity we have assumed that no electrophilic assistance (rather than a very small degree of such assistance) operates for the aryl—silicon compounds; the weight of evidence now seems to point to this [3], but the existence of some electrophilic assistance offers the only explanation at present for the substituent effects in $XC_6H_4SiMe_3$ compounds [5].

Results and discussion

We used three types of media for which the H_- acidity functions [8a] are known, and which involve mixtures of varying amounts of hydroxylic species with an inert species, viz. $Me_2SO/MeOH/MeONa$ (0.01 *M*) (I) [8b], $Me_2SO/EtOH/EtONa$ (0.01 *M*) (II) [9] and $Me_2SO/H_2O/HONMe_4$ (III) [10]. (For medium I, aniline and diphenylamine type indicators were used in the H_- determinations, and for II carbon acid indicators). In most cases we have had to use H_- data for 25° C in conjunction with rate constants measured at 50° C, but this does not affect the validity of the qualitative discussion below.

Observed pseudo first order rate constants *k* are listed in Table 1. With one exception we observed an acceptably linear relationship between log *k* and H_- for the methanolic medium I, for which the data are most extensive. The exception was provided by the 9-fluorenyl- compound, for which there is a deviation from linearity at very low DMSO contents; while the linearity is acceptable with a slope of ca. 1.05, in media containing >4 mole % of DMSO, as used for most other compounds, the initial slope starting from the wholly methanolic medium is ca. 1.4. Since we are interested in comparisons, the slope of 1.05 will be used for this compound in the subsequent discussion. Some representative plots are shown in Fig. 1, and the approximate slopes of the plots for all the compounds are listed in Table 2.

For the methanol-containing medium, I, there are three significant features of the results as follows: (a) for the silicon compounds the slopes (mostly based on rate constants measured at 50° C) are in the range 0.95—1.2; (b) for the tin derivatives, the compounds with R = m-$ClC_6H_4CH_2$ and 2-C_8H_5S give markedly smaller slopes (0.7 and 0.45, respectively) than their silicon analogues; (c) the slope (1.2) for the tin compound with R = Ph_2CH is substantially larger than that for the other tin derivatives, and is essentially the same as that for the corresponding silicon compound. Features (a) and (b) are consistent with, and would be expected to follow from, the proposed mechanistic differences. If the near unity slopes for the silicon compounds are associated with generation of a free carbanion in the rate-determining step (such an association would be expected in the ideal case), then smaller slopes would be expected for the tin compounds, since the effect of the increasing basicity of the medium as the methanol content is lowered would be offset by the decreased availability of the methanol to provide electrophilic assistance. That the slope for the tin compound with R = Ph_2CH should be close to that for the silicon compound suggests that the electrophilic assistance mechanism, A (or possibly A_s) may have given way to the type B (or possibly B_s) mechanism which applies to the silicon compounds, a possibility which we have foreseen [3]. It is thus especially interesting that preliminary results on solvent isotope effects for cleavage of this tin compound are, indeed, consistent with a type B mechanism [11].

For the tin compounds $Me_3SnC_8H_5S$-2, $Et_3SnC_8H_5S$-2, $Me_3SnCH_2C_6H_4Cl$-m, and i-$Pr_3SnC_8H_5S$, the slopes fall as the product isotope effect, PIE in methanol rises. (The PIE values are 0.44, 0.60, 0.70, and 0.72, respectively [3].). Increase in the PIE values is thought to reflect increase in the degree of proton transfer at the transition state of a mechanism of type A [1—3], and thus the parallelism of the slopes and PIE values is consistent with the observed correlation between

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TABLE 1

PSEUDO FIRST ORDER RATE CONSTANTS FOR CLEAVAGE OF R'_3MR COMPOUNDS IN $Me_2SO/MeOH/MeONa$ (0.01 *M*), (I), $Me_2SO/EtOH/EtONa$ (0.01 *M*), (II), and $Me_2SO/H_2O/Me_4NOH$ (0.011 *M*), (III), at 50°C

R'_3M	R	Medium I			Medium II			Medium III		
		$[Me_2SO]$ (mole %)	$10^5 k$ (s^{-1})	H_-[a]	$[Me_2SO]$ (mole %)	$10^5 k$ (s^{-1})	H_-[a]	$[Me_2SO]$ (mole %)	$10^5 k$ (s^{-1})	H_-[a]
Me_3Si	*m*-$ClC_6H_4CH_2$	47.58	149	14.92	31.20	25.33	15.46	27.77	86.5	15.28
		36.31	19.5	14.20	23.90	7.2	15.10	22.55	25.2	14.71
		27.52	3.9	13.65	15.7	1.84	14.74			
Me_3Si	Ph_2CH	47.58	718 [b]	14.92	31.20	71.5	15.46	27.77	113	15.28
		36.31	156 [c]	14.20	23.90	26	15.10	22.55	295	14.71
		27.52	46 [d]	13.65	15.71	8.7	14.72			
Me_3Si	*p*-$NO_2C_6H_4CH_2$	17.24	1030 [f]	13.01						
		8.08	285 [f]	12.44						
		4.34	158 [f]	12.20						
		0.0	76.5 [f]	11.94						
Me_3Si	9-fluorenyl	17.24	1410 [f]	13.01						
		11.48	640 [f]	12.65						
		8.11	380 [f]	12.44						
		4.29	195 [f]	12.20						
		1.78	114 [f]	12.05						
		0	73.5 [f]	11.94						
Me_3Si	2-benzothienyl	47.58	440	14.92	31.20	153	15.46	22.55	200	14.71
		43.25	210	14.64	23.90	45	15.10	17.62	70	14.08
		36.31	63	14.20	15.71	11.7	14.72	9.14	15.6	13.04
		27.52	14.1	13.65						
		0	0.115 [e]	11.94						

Me_3Sn	m-$ClC_6H_4CH_2$	47.58	18.5	14.92	23.90	14.7	15.10	27.77	103	15.28
		36.31	5.8	14.20	15.71	7.6	14.72	22.55	48.5	14.71
		27.52	2.4	13.65	31.20	25.8	15.46			
	Ph_2CH	27.52	440 [a]	13.65	15.71	1360 [a]	14.72			
		17.24	76.5 [a]	13.01	11.20	605 [a]	14.51			
		11.48	29.8 [a]	12.65	6.08	238 [a]	14.28			
		0	4.1 [a]	11.94						
	2-benzothienyl	43.25	740 [a]	14.64	23.90	370 [a]	15.10	9.14	1090 [a]	13.0
		35.52	420 [a]	14.16	15.71	210 [a]	14.72			
		27.52	230 [a]	13.65	11.20	141 [a]	14.51			
		25.52	200 [a]	13.53	6.08	91 [a]	14.28			
		20.31	145 [a]	13.20	0.00	44 [a]	14.00			
		13.91	92 [a]	12.80						
		9.67	76 [a]	12.53						
		0.0	42 [a]	11.94						
		11.48	475	12.65						
		8.1	380	12.44						
		0	240	11.94						
Et_3Sn	2-benzothienyl	47.58	89 [a]	14.92						
		43.25	60 [a]	14.64						
		36.31	33 [a]	14.20						
		27.52	15.6 [a]	13.65						
i-Pr_3Sn	2-benzothienyl	47.58	4.3	14.92						
		43.25	2.75	14.64						
		39.42	1.89	14.40						
		0	0.03 [c]	11.94						

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[a] At 25°C; [b] $10^5\,k = 114\ s^{-1}$ at 25°C; [c] $10^5\,k = 21\ s^{-1}$ at 25°C; [d] $10^5\,k = 5.1\ s^{-1}$ at 25°C. [e] Approximate value derived from rate at a different base concentration. [f] At 20°C.

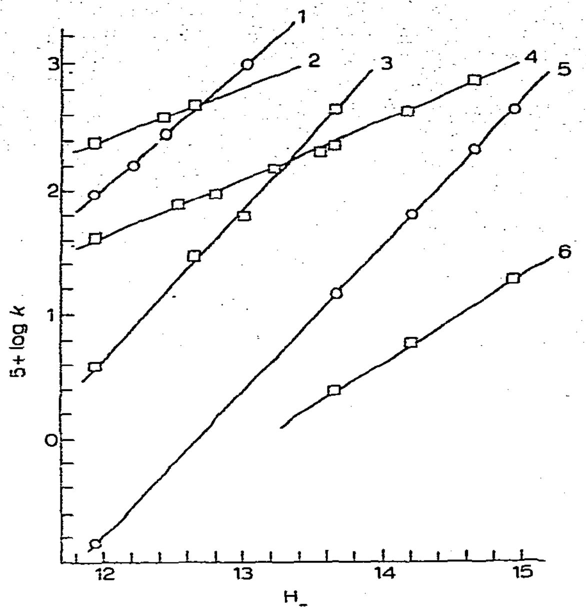

Fig. 1. Plots of 5 + log *k* against H_- for 1, $Me_3SiCH_2C_6H_4NO_2$-*p* (at 20°C); 2, $Me_3SnC_8H_5S$-2 (at 50°C); 3, $Me_3SnCHPh_2$ (at 50°C); 4, $Me_3SnC_8H_5S$-2 (at 25°C); 5, $Me_3SiC_8H_5S$-2 (at 50°C); 6, $Me_3SnCH_2C_6H_4Cl$-*m* (at 50°C).

such slopes and the values of the Brønsted β_{OH^-} coefficients in simple proton transfers from carbon [12,8b].

Linear plots, usually based on three points, were obtained in the other media for a few compounds. The slopes are very different from those obtained with medium I. Compared with those in medium I, the slopes were in general marked-

TABLE 2

SLOPES OF LOG *k* — H_- PLOTS FOR R'_3MR COMPOUNDS IN $Me_2SO/MeOH/MeONa$, (I), $Me_2SO/EtOH/EtONa$, (II), AND $Me_2SO/H_2O/HONMe_4$, (III)

R'_3M	R	Temp (°C) [a]	I	II	III
Me_3Si	*m*-$ClC_6H_4CH_2$	50	1.22	1.52	1.20
	Ph_2CH	25	1.08		
		50	0.95	1.26	0.96
	p-$NO_2C_6H_4CH_2$	20	1.04		
	9-fluorenyl	20	1.05 [b]		
	2-benzothienyl	50	1.18	1.50	0.67
Me_3Sn	*m*-$ClC_6H_4CH_2$	50	0.70	0.73	0.76
	Ph_2CH	25	1.16	1.67	
	2-benzothienyl	25	0.48	0.80	
		50	0.44		
Et_3Sn		25	0.60		
i-Pr_3Sn		50	0.72		

[a] Temperature at which *k* was measured. The H_- values are for 25°C. [b] See text.

ly higher in ethanol-containing medium II, and somewhat lower in the water-containing medium III. The slopes could reasonably be expected to be closest to unity for the silicon compounds in medium II, since carbon acids were used as the H_- indicators in this case [9],but, in fact, in two of the three cases studied they are substantially larger. In the few cases studied the slopes in medium III are fairly similar to those in medium I, except for 2-benzothienyltrimethylsilane, which gives a surprisingly low slope in medium III.

The changes of rate on going from one medium to another cannot be related to the H_- values even when attention is confined to the silicon compounds. Since the slopes of the log k — H_- plots are so different, the relative rates for a compound in the three media at a fixed H_- depend greatly on the particular H_- value taken. Even though in all cases rates in the range of H_- values actually used were substantially smaller at a given H_- for the ethanol-containing medium II than for the other two, extrapolation indicates that this would not remain so at much higher H_- values because of the large slopes in medium II. It is probably significant that for the compounds with $R = m\text{-}ClC_6H_4CH_2$, the rate is several times lower for medium I than for medium III in the case of the tin compound while the reverse is true for the silicon compound. (Approximate values of 10^5k of 21 and 80 s^{-1} in media I and III, respectively, can be derived at $H_- = 15$ for M = Sn, and corresponding values of 200 and 60 s^{-1} for M = Si.) Two factors could account for this: (a) at a given H_-, the concentration of water in medium III is higher than that of methanol in medium I, and, more importantly, water is a better proton donor than methanol. Thus the water-containing medium should favour the reaction of the tin compound, for which electrophilic assistance is required, over that of the silicon compound.

We previously noted that whereas tin compounds with $R = XC_6H_4$ are very much more reactive than the corresponding silicon compounds in methanol or aqueous methanol, the silicon compound with $R = C_6H_5$ becomes more reactive than the corresponding tin compound in $Me_2SO/H_2O/NaOH$ containing small proportions of water [13]. We interpreted this in terms of the need for electrophilic assistance in the case of the tin compound, since this assistance would be less available at low water concentrations in the Me_2SO/H_2O mixtures [2,5,13]. The data in Tables 1 and 2 show that this behavour probably represents a general trend. The lower slopes for the tin compounds in all three media imply that the rates increase less rapidly for those for silicon compounds as the proportion of the hydroxylic component of the medium is lowered, so that a silicon compound which is markedly less reactive than the corresponding tin compound in, say, pure methanol or aqueous-methanol may become the more reactive in media of very high DMSO content.

Experimental

Organometallic Compounds. These are all known compounds, and pure samples used for previous studies [1—3,5,14] were taken.

Media. Dimethyl sulphoxide was dried by distillation from calcium hydride at reduced pressure (<50° C) and was stored under nitrogen. Methanol and ethanol were refluxed over magnesium turnings after addition of a crystal of iodine, and then fractionated from the mixture.

Sodium alkoxide solutions were obtained by dissolving clean sodium in the purified alcohols, and weighed amounts of solutions of the appropriate strength were mixed with DMSO to give a 0.020 *M* solution. The organometallic compound was dissolved in an alcohol/DMSO mixture of the same composition, and for rate measurements a sample of this solution was mixed with an equal volume of the alkoxide solutions to give a base concentration of 0.010 *M*. A similar procedure starting with aqueous tetramethylammonium hydroxide was used for medium III.

The progress of the reaction was followed spectrophotometrically as previously described [3,15]. Good first-order plots were obtained, and rate constants were reproducible to within 3% in runs using different batches of the stock solutions. The spectra at the completion of the reactions agreed with those of the expected cleavage products.

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