Kinetic Isotope Effects for Proton Abstraction from Methanol by Polyhalogenomethyl Carbanions. Cleavage of Me_3SiCHX_2 and Me_3SiCX_3 by Base in Methanol

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The carbanions $X_xH_{(3-x)}C^-$(X = Cl or Br; x = 2 or 3) generated by base cleavage of $Me_3SiCH_{(3-x)}X_x$ (or some related compounds) in MeOH, show a kinetic isotope k_H/k_D of *ca.* 1.1 in proton abstraction from methanol, as given by the product ratio $X_xH_{(3-x)}CH/X_xH_{(3-x)}CD$ observed for reaction in MeOH–MeOD (1 : 1) at *ca.* 21 °C. The low value of the isotope effect is attributed to the fact that the free electron pair in the carbanion is localized on the carbon centre; carbanions derived from acids of acidities comparable with those of X_3CH and X_2CH_2 but in which the electron pair is conjugatively delocalized, show much larger isotope effects

It is known that cleavage by base in methanol or aqueous methanol of the Si–R bond in compounds of the type Me_3SiR, where RH is a carbon acid, involves rate-determining generation of the carbanion R^-, which then reacts rapidly with the solvent to give RH.[1–5] The ease of cleavage is related to the stability of the forming carbanion and so to the acidity of RH and (in the absence of serious steric effects at the carbon centre[6]) the value of log k_s, where k_s is the specific rate constant (the observed first-order rate constant divided by the base concentration), is linearly related to the pK_a of RH.[7] (The pK_as used for this system were those determined for solutions in cyclohexylamine,[8] since the range of relevant data is available only for that medium. The implication is that the relative pK_a values for the acids RH are much the same in MeOH, or that the values in the two media are linearly related.)

Since the great majority of carbon acids of appropriate acidity are those that give conjugatively delocalized anions, most of the cleavage studies have been concerned with compounds Me_3SiR derived from such acids, and for these it has been shown that the value of the product isotope effect, PIE, given by the ratio RH:RD of the products formed in a 1:1 mixture of MeOH and MeOD (and reflecting the relative rates of hydron abstraction from MeOH and MeOD), rises with the acidity of RH (and would be expected to pass through a maximum for species derived from acids stronger than those so far used). Thus with substituted benzyltrimethylsilanes and trimethylsilyl derivatives of di- and tri-phenylmethane, fluorene (pK_a 22.85), and indene (pK_a 19.93) the pie rises from *ca.* 1.1 to *ca.* 10, in line with the ease of cleavage.[2,*] Values of *ca.* 9–10, are found, for example, for $Me_3SiCH_2C_6H_4NO_2$-*p*, 9-trimethylsilylfluorene, and 1-trimethylsilylindene.

However, a high acidity of RH, and thus a high rate of cleavage of Me_3SiR, is not a sufficient condition for generation of high pie values. Thus, for a range of 2-trimethylsilylthiophenes, 2-Me_3Si-C_4H_2S-X, the rates of cleavage correspond with pK_as of *ca.* 38–15, but the observed pie values all fall within the range 1.0–1.2 (and can probably be regarded as effectively constant at 1.1 ± 0.1).[4] This can be attributed to the fact that there is little, if any, conjugative delocalization of the free electron pair in the thienyl anions, and so the proton is transferred to the anion without the need for the substantial reorganization of the bond structure that is necessary in the case of conjugatively delocalized anions (and the transfer thus much faster than that to the latter anions). Subsequently Kresge and his colleagues also suggested that carbanions R^- with localized electron pairs might be protonated very rapidly and the corresponding acids RH thus show 'normal' behaviour (in the Eigen sense[10]) as distinct from the pseudo-acid behaviour observed for most carbon acids.[11] They found support for their view in the nature of the Brönsted relations for detritiation of phenylacetylene and chloroform,[11] and later in the case of chloroform in the low value of the isotope effect for transfer of a hydron from Cl_3CH (k_H/k_D 1.48) to hydroxide ion in water, but found that phenylacetylene could behave either as a normal or as a pseudo acid depending upon the strength of the base to which the proton was being transferred.[12]

The simplest carbon acids of relevant acidity in which the acidity is not due to conjugative delocalization are the halogenomethanes, $X_xCH_{(4-x)}$ (x = 2, 3) and we thus thought it of interest to examine the reactivities and pie values for the compounds Me_3SiCHX_2 and Me_3SiCX_3 (X = Cl or Br) in the cleavages. For comparison, pie values were also determined for some related compounds with other inert substituents on silicon and for some analogous germanium compounds.

Results and Discussion

We first compared the rates of cleavage of $Me_3SiCHCl_2$ and $Me_3SiCHBr_2$ with that of 9-fluorenyltrimethylsilane (9-$FlSiMe_3$) in NaOMe–MeOH at 25 °C, and at the same time determined the rate isotope effect, RIE, given by the ratio of the values of k_s in MeOH and MeOD, respectively. The results are shown in Table 1, and it is seen that $Me_3SiCHCl_2$ and $Me_3SiCHBr_2$ are cleaved *ca.* 0.17 and 17 times as rapidly as 9-$FlSiMe_3$, implying (*cf.* refs. 2 and 3) pK_a values of *ca.* 25 and 19 (on the scale used) for CH_2Cl_2 and CH_2Br_2, respectively. If the pie's were thus related directly to the pK_a of RH or to the rate of cleavage of Me_3SiR, pie values in the region of 9 or 10, respectively, would be expected for R = $CHCl_2$ or $CHBr_2$.

We could not make a direct comparison of the rates of cleavage of Me_3SiCCl_3 and Me_3SiCBr_3 with those of the usual reference compounds because even in MeOH alone the reaction was too fast for study by our methods, and only when 0.002 mol

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[*] For some pyridyl- and quinolyl-methyl(trimethyl)silanes the pie's were found generally to rise with the ease of cleavage from *ca.* 1.1 to *ca.* 5.6, but were lower than for $Me_3SiCH_2C_6H_5X$ compounds of comparable reactivity, indicating that the relationship between pie and rate of cleavage cannot be quantitatively carried over from one series of compounds generating delocalized carbanions to another.[9]

Table 1 Rates and rate isotope effects in cleavage of $Me_3SiCHCl_2$ and $Me_3SiCHBr_2$ in MeOH–MeOD (1:1) at 25.0 °C

Organosilane	Solvent	$[MeONa]/10^{-3}$ mol dm^3	$k/10^{-4}$ s^{-1}[a]	k_s/dm^3 mol^{-1} s^{-1}[b]	rie[c]
$Me_3SiCHCl_2$	MeOH	5.2	0.78	0.015	0.50
$Me_3SiCHCl_2$	MeOD	5.5	1.76	0.032	—
$Me_3SiCHBr_2$	MeOH	4.2	63	1.5	0.52
$Me_3SiCHBr_2$	MeOD	4.0	120	3.0	—
9-Trimethyl silylfluorene	MeOH	5.2	4.6	0.088	—

[a] Observed first-order rate constant. [b] Specific rate constant (k/[MeONa]). [c] Value of k_s in MeOH divided by that in MeOD

Table 2 Values of the product isotope effect, pie, for cleavage of some di- and tri-halogenomethyl derivatives of silicon and germanium by *ca.* 0.001 mol dm^{-3} NaOMe in MeOH–MeOD (1:1) at *ca.* 21 °C

Substrate	pie	Substrate	pie
$Me_3SiCHCl_2$	1.10	$(MeO)_3SiCHCl_2$	1.18
$PhMe_2SiCHCl_2$	1.19	$Me_3SiCMeCl_2$	1.18
p-$ClC_6H_4SiCHCl_2$	1.13	$Me_3SiCHBr_2$	1.19
p-$MeOC_6H_4SiCHCl_2$	1.11	$\overline{CH_2(CH_2)_2Si}(Me)CHBr_2$	1.20
p-$MeC_6H_4SiCHCl_2$	1.11	Me_3SiCCl_3	1.07
m-$ClC_6H_4SiCHCl_2$	1.09	Me_3SiCBr_3	1.17
m-$CF_3C_6H_4SiCHCl_2$	1.09	Me_3GeCCl_3	1.07
$(MeO)Me_2SiCHCl_2$	1.12	Me_3GeCBr_3	1.15

[a] Estimated standard deviation based on reproducibility, 0.04

dm^{-3} CF_3CO_2H was present was the concentration of MeO^- low enough to give a measurable rate. Under these conditions the observed first-order rate constants are 3.6×10^{-6} and 2.1×10^{-3} s^{-1}, respectively. (There was no detectable cleavage when 0.2 mol dm^{-3} CF_3CO_2H was present, confirming that there is no cleavage by MeOH as distinct from MeO^-.) The specific rate constant for Me_3SiCCl_3 is thus several orders of magnitude greater than that for 1-indenyltrimethylsilane (the pK_a of indene is 19.9), and reasonably consistent with the pK_a for $CHCl_3$ of 15 derived polarographically[13] or of 15.5 derived from the rates of hydrogen exchange in Me_2SO–H_2O.[14,*] The factor of *ca.* 580 between the rates for Me_3SiCBr_3 and Me_3SiCCl_3 seems remarkably large, and our usual assumptions would correspond to a pK_a difference of *ca.* 9 units, substantially greater than the difference of 6 units derived polarographically (pK_a for $CHBr_3$, 9)[13] and much greater than that of 2 units estimated from kinetic data.[14]

Whatever the actual values of k_s for the cleavage of Me_3SiCCl_3 or Me_3SiCBr_3 or of the relevant pK_as for $CHCl_3$ and $CHBr_3$, they are evidently in the range in which high pie values would be expected if we were dealing with systems involving delocalized carbanions (though they might be a little beyond the maximum expected for such carbanions).

Values of the pie were obtained by adding 0.1 cm^3 of a *ca.* 0.6 mol dm^{-3} solution of Me_3SiR or related compound in MeOH–MeOD (1:1) to 0.7 cm^3 of an 0.008 mol dm^{-3} solution of NaOMe in the same medium at room temperature (*ca.* 21 °C), and after 30 s extracting the organic material and determining the ratio RH:RD by mass spectrometry. (It is shown below that no appreciable hydrogen exchange could have taken place in the cleavage products before the analysis.) The results are shown in Table 2; the estimated standard deviations shown are more a measure of the reproducibility than of absolute accuracy, and we think that the apparent variations are not significant, and that a general value of 1.1 ± 0.1 can be assumed. It is evident that, as predicted on our previous reasoning,[4] there is a value of near unity for the isotope effect k_H/k_D for abstraction of a hydron from MeOH by any of the anions Cl_3C^-, Cl_2HC^-, Br_3C^- and Br_2CH^-. The result is consistent with the finding by Kresge and his colleagues of a low value for the isotope effect for the reverse hydron transfer.[12]

Aspects of the Cleavage of Me_3SiCCl_3 *and* $Me_3SiC{\equiv}CPh$.—In order to confirm that there could be no interference from hydrogen exchange in the initial products formed from Me_3CSiCl_3 under the conditions used for the determination of the pie values we measured the rate of dedeuteriation of Cl_3CD in MeONa–MeOH (0.050 mol dm^{-3}) at 25 °C, and obtained a first-order rate constant of 4.3×10^{-4} s^{-1}. This corresponds to a half-life of *ca.* 27 min at a base concentration 50 times that used for the measurement of pie values.

The rate of cleavage of Me_3SiCCl_3 in a given MeONa–MeOH medium is evidently several powers of ten (probably $> 10^5$) greater than that of dedeuteriation of Cl_3CD. The behaviour is consistent with that observed for cleavage of all other Me_3SiR compounds, where RH is a carbon acid, except $Me_3SiC{\equiv}CPh$ (and its derivatives), for which the cleavage[6,15] is slower by several powers of ten than hydrogen exchange[16] in $PhC{\equiv}CH$. (This, of course, prevents determination of the pie for the cleavage.) In this respect $Me_3SiC{\equiv}CPh$ resembles the compounds Me_3SiX derived from even very weak 'normal' acids such as HOMe, H_2S, and the acetylene analogue $HC{\equiv}N$ (*cf.* refs. 4 and 6). We previously suggested that the anomalous relationship between the rate of cleavage of $Me_3SiC{\equiv}CPh$ and that of hydrogen exchange in $PhC{\equiv}CH$ might be attributable to steric hindrance to solvation of the carbanion being formed from $Me_3SiC{\equiv}CPh$, in which the forming electron pair is located between the carbon and silicon atoms (in contrast to the situation for forming conjugatively-delocalized carbanions).[6] However, this explanation would imply that the rate of cleavage of $Me_3SiC{\equiv}CPh$ is abnormally low compared with that of other Me_3SiR species derived from acids RH of similar acidity, but in fact the value of log k_s for the cleavage of $Me_3SiC{\equiv}CPh$ by base in H_2O–MeOH falls well on the plot of log k_s *vs.* pK_a when the pK_a of 23.24 in cyclohexylamine is used.[7] Moreover, there should be similar steric hindrance to solvation in cleavage of Me_3SiCCl_3, whereas, as usual, the cleavage is much faster than the exchange. An alternative explanation, that there may be substantial stabilization of $Me_3SiC{\equiv}CPh$ by conjugative interaction with the Me_3Si group [either by $(p{\rightarrow}d)_\pi$ bonding or negative hyperconjugation[17]] also runs into the objection that the rate of cleavage is in line with the pK_a of $PhC{\equiv}CH$. It seems from our results that it is the very high rate of the exchange that is abnormal (the rate being much higher than would be expected from comparison of its equilibrium pK_a with those for acids giving delocalized anions). This could, indeed, be expected if $PhC{\equiv}CH$ behaved as a normal acid, but Kresge and his colleagues have shown that it must be classified as a pseudo-acid under some conditions in which Cl_3CH behaves as a normal acid,[12] and yet the cleavage–exchange rate relationship is apparently normal for the Cl_3C compounds. Possibly a simpler

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[*] From kinetic data Kresge and his colleagues have estimated the absolute pK_a of $CHCl_3$ in H_2O to be *ca.* 24.[12]

way of looking at the anomaly is to note that the cleavage of $Me_3SiC{\equiv}CPh$ is much slower than that of Me_3SiCCl_3 whereas exchange in $PhC{\equiv}CH$ is much faster than that in Cl_3CH, and we can offer no satisfactory explanation for this.

Experimental

Preparations.—The compounds Me_3SiCHX_2[18,19] and Me_3SiCX_3 (X = Cl or Br),[20] $XC_6H_4Me_2SiCHCl_2$,[21] $MeOMe_2SiCHCl_2$,[22] $(MeO)_3SiCHCl_2$,[22] $Me_3SiCMeCl_2X]$,[23] $\overline{CH_2(CH_2)_2Si}(Me)CHBr_2$,[20] and Me_3GeCX_3 (X = Cl or Br),[24] were prepared as previously described.

Rate Measurements.—The rate constants for cleavage of Me_3SiCHX_2 and Me_3SiCX_3 (X = Cl or Br) were determined by GLC analysis of the reaction mixture as previously described for related compounds[2,5] and those for cleavage of 9-fluorenyltrimethylsilane were determined spectrophotometrically.[2] The rate constant for dedeuteriation of $CDCl_3$ was determined by adding *ca.* 1 μmol of $CDCl_3$ (>99.5% D) from a microsyringe to a solution of NaOMe–MeOH (0.9 cm^3; 0.050 mol dm^{-3}) containing benzene (0.185 μmol) as internal reference and preheated to 25 °C. The tube was shaken then placed in the probe (kept at 25.0 ± 0.5 °C) of a Bruker AS 200 MHz spectrometer and the ^1H NMR spectrum was recorded automatically every 5 min. The rate of appearance of $CHCl_3$ was determined from relative integrals of the peaks from C_6H_6 and $CHCl_3$. An excellent first order plot was obtained.

Product Isotope Effect Determinations.—To a solution of the substrate in 1:1 MeOH–MeOD (0.1 cm^3; 0.6 mol dm^{-3}), in a dry-box, was added (from a syringe), at room temperature (*ca.* 21 °C), a solution of NaOMe (0.7 cm^3; 0.008 mol dm^{-3}) in the same medium. After 30 s the mixture was shaken with a mixture of CCl_4 (2 cm^3) and water (1 cm^3) and the CCl_4 layer was separated and dried (Na_2SO_4). A sample was injected into a gas chromatograph (1.5 m of 10% OV-101 on Chromasorb Q; temperature raised at 10 °C min^{-1} from 40–200 °C) linked to an LKB mass spectrometer. The ratios of the heights of the components of the M^+ peak pattern (*e.g.* those at *m*/*z* 84 and 85, 86 and 87, and 88 and 89 for $CHCl_2$ and $CDCl_2$) gave the relative amounts of deuteriated and undeuteriated compounds; the ratios from the various pairs of peaks were in excellent agreement.

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