

Base Cleavage of the Benzyl-Silicon Bonds in $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ and $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$. Proposed Formation of Metasilicate Intermediates

Jadwiga Chmielecka, Julian Chojnowski,* and Włodzimierz A. Stańczyk

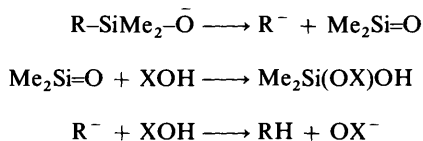
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, 90-362 Łódź, Poland

Colin Eaborn*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

A kinetic study of the base-catalysed cleavage of the diol $\text{RSiMe}(\text{OH})_2$ ($\text{R} = m\text{-ClC}_6\text{H}_4\text{CH}_2$) in $\text{Me}_2\text{SO-H}_2\text{O}$ or $\text{MeOH-H}_2\text{O}$ has indicated that at high base concentrations the main process is the unimolecular dissociation of the dianion $\text{RSiMe}(\text{O}^-)_2$ into R^- and $\text{Me}(\text{O}^-)\text{Si=O}$ (an analogue of acetate ion), both of which then react rapidly with the solvent. Likewise for the triol $\text{RSi}(\text{OH})_3$ in $\text{Me}_2\text{SO-H}_2\text{O}$ the main process appears to be the formation of R^- and the metasilicate ion $\text{HO}(\text{O}^-)\text{Si=O}$ from the dianion $\text{R}(\text{OH})\text{Si}(\text{O}^-)_2$. Base cleavage of the silanols RSiMe_2OH ($\text{R} = \text{PhCH}_2$ or $m\text{-ClC}_6\text{H}_4\text{CH}_2$) in $\text{Me}_2\text{SO-H}_2\text{O}$ probably involves a contribution from the unimolecular dissociation of the anion RSiMe_2O^- to give R^- and $\text{Me}_2\text{Si=O}$.

We previously suggested that when the compounds RSiMe_2OMe ($\text{R} = m\text{-ClC}_6\text{H}_4\text{CH}_2$ or $\text{PhC}\equiv\text{C}$) are dissolved in 5% v/v $\text{H}_2\text{O-MeOH}$ containing NaOH the cleavages of the R-Si bonds involve concurrent reactions of the neutral species RSiMe_2OMe and RSiMe_2OH and the anionic species RSiMe_2O^- .¹ Thus the value of the observed first-order rate constant k_{obs} is thought to be the sum of the pseudo-first-order rate constants for cleavage by attack of OH^- (and OMe^-) on the silicon atom of RSiMe_2OMe and RSiMe_2OH and the first-order rate constant for spontaneous, *i.e.* unimolecular, cleavage of the RSiMe_2O^- anion, in a process, depicted below ($\text{X} = \text{H}$ or Me), involving a silanone intermediate:



For those cleavages, the plot of the observed first-order rate constant k_{obs} against the base concentration $[\text{OH}^-]$ initially rises steeply with increase in the base concentration then curves off to an almost constant value of k_{obs} . At the higher base concentrations the value of k_{obs} remains approximately constant because (a) almost all the RSiMe_2OMe is converted *via* RSiMe_2OH into RSiMe_2O^- ; (b) additional base has little effect on the concentration of RSiMe_2O^- (while substantially lowering the concentration of RSiMe_2OMe and RSiMe_2OH); and (c) an increase in the base concentration which halves the combined amount of the neutral species (RSiMe_2OMe and RSiMe_2OH) at the same time roughly doubles the rate at which the remaining half reacts, and so the contribution from the bimolecular cleavage is approximately constant. The experimental result could be very satisfactorily interpreted in terms of this picture, and on reasonable assumptions it appeared that the contributions by the unimolecular decomposition of the RSiMe_2O^- species were substantial, but it was recognised that plot of k_{obs} against $[\text{OH}^-]$ would have the same form even if only cleavages of the neutral species were significant.¹ There is, however, strong independent evidence, based on the abnormally high reactivity of $[(\text{Me}_3\text{Si})_3\text{C}]\text{SiPh}(\text{OH})\text{I}$ in the presence of base, for ejection of an anionic ligand from a silanolate ion to give a silanone.^{1a,2}

To throw further light on the mechanism of base cleavage of RSiMe_2OH compounds we decided to examine such reactions in $\text{H}_2\text{O-Me}_2\text{SO}$ (in which there would be no complication arising from the presence of other neutral species such as RSiMe_2OMe), and later extended the study to cleavages of $\text{RSiMe}(\text{OH})_2$ and $\text{RSi}(\text{OH})_3$ species. The results are described below. (For a preliminary report see ref. 3.)

Results and Discussion

We first examined the cleavages of the compounds $\text{PhCH}_2\text{SiMe}_3$ and $\text{PhCH}_2\text{SiMe}_2\text{OH}$ (generated *in situ* from $\text{PhCH}_2\text{SiMe}_2\text{OMe}$) in 1:1 and 3:1 v/v $\text{Me}_2\text{SO-H}_2\text{O}$. As expected, the values of the observed first-order rate constants k_{obs} for cleavage of $\text{PhCH}_2\text{SiMe}_3$ were much higher in these media, especially in the less aqueous one, than for those in $\text{H}_2\text{O-MeOH}$; the ratios of the rate constants for 0.2 mol dm^{-3} base in MeOH , 1:1, and 3:1 $\text{Me}_2\text{SO-H}_2\text{O}$ are *ca.* 1:100:40 000. The ratios are reasonably in line with the increase in the basicities of the solutions, as indicated by the values of acidity function h_- (where the more usual acidity function H_- is equal to $-\log h_-$), which are roughly in the ratio 1:10²:10⁴ for 0.01 mol dm^{-3} base in the three media;^{4,5} such dependence of the rate of cleavage of RSiMe_3 compounds on the acidity function has been observed previously for cleavages in other media.⁶

In order to investigate the possibility that the basicities of solutions of KOH in the $\text{Me}_2\text{SO-H}_2\text{O}$ media, and thus the rates of cleavage in processes involving nucleophilic attack by OH^- on silicon, might depart seriously from a linear dependence on the base concentration in the range used in the present studies (as do those of solutions of base in alcohols at high base concentrations), we determined first-order rate constants k for cleavage of $\text{PhCH}_2\text{SiMe}_3$ in 3:1 $\text{Me}_2\text{SO-H}_2\text{O}$ containing 0.675×10^{-2} – 12.7×10^{-2} mol dm^{-3} KOH . The results are shown in Table 1, and it will be seen that the value of the specific rate constant $k/[\text{KOH}]$ falls progressively by a factor of almost two as the base concentration is increased, but this variation is small enough to justify the approximation made in the later discussion that the basicities in the $\text{Me}_2\text{SO-H}_2\text{O}$ media are proportional to the base concentration. It is of interest that the values of k , and thus presumably the basicities of the solutions, increase with base concentration less than would be expected for simple proportionality, whereas in alcohols the basicities

and rates of cleavage increase more rapidly with base concentration than would be expected on that basis. It is also noteworthy that in the cleavage in 3:1 Me₂SO-H₂O, replacement of KOH by NaOH has little effect on the value of *k*. From measurements of *k* at 25 and 30 °C at one base concentration, approximate values of 15 kcal mol⁻¹ and -21 cal mol⁻¹ K⁻¹ can be derived for the energy and entropy of activation, respectively, and these are consistent with a bimolecular process.

Values of the observed first-order rate constant *k*_{obs} at various base concentrations for cleavage of PhCH₂SiMe₂OH in 1:1 and 3:1 Me₂SO-H₂O, are shown in Table 2. Plots (not shown) of *k*_{obs} against the base concentration have the same general form as those observed for the cleavages in H₂O-MeOH mentioned earlier, *i.e.* the observed rate constant curves off towards a constant value as PhCH₂SiMe₂OH is progressively converted into RSiMe₂O.

As shown previously for reactions in MeOH-H₂O,¹ if the basicity is assumed to increase linearly with the base concentration, then the value of *k*_{obs} in the Me₂SO-H₂O medium concerned will be given by equation (1), where *k*_{AOH} is the (second-order) rate constant for the neutral species RSiMe₂OH (subsequently denoted by AOH), *k*_{AO⁻} the first-

order rate constant for unimolecular cleavage of RSiMe₂O⁻ (subsequently denoted by AO⁻), and *r* the fraction of RSiMe₂-OH converted into RSiMe₂O⁻ (*i.e.* $r = [\text{AO}^-]/([\text{AO}^-] + [\text{AOH}])$). This can {since $[\text{AO}^-]/[\text{AOH}] = r/(1-r)$ } be transformed into equation (2), where *K* is $[\text{AO}^-]/([\text{AOH}]-[\text{OH}^-])$.

$$k_{\text{obs}} = k_{\text{AOH}}(1-r)[\text{OH}^-] + rk_{\text{AO}^-} \quad (1)$$

$$k_{\text{obs}} = \{(k_{\text{AOH}}/K) + k_{\text{AO}^-}\}r \quad (2)$$

Thus the plot of *k*_{obs} against *r* should be linear, with a slope related to the values of *k*_{AOH}, *k*_{AO⁻}, and *K*. When approximate values of *K* determined spectroscopically (see below) are used to determine values of *r*, the plots (not shown) of *k*_{obs} against *r*, are indeed linear for both media, and from their slopes, values of *k*_{AOH} and *k*_{AO⁻} can be estimated as described below.

Approximate values of *K* of 13 and 200 dm³ mol⁻¹, respectively, were derived for PhCH₂SiMe₂OH in 1:1 and 3:1 Me₂SO-H₂O by observing the change in the u.v. spectrum of solutions of the silanol containing various amounts of KOH (see the Experimental section). The 15-fold increase in *K* on going from the 1:1 to 3:1 medium might at first sight seem rather small in view of the increase in *h*₋ by a factor of *ca.* 10², but the acidity functions were determined with amines that would give highly delocalized anions, which are hydrated much less effectively than hydroxide ions in water, and so are much less affected by the decrease in solvation on going to the less aqueous media. The hydration of silanolate ions, however, as of alkoxide ions with essentially localized charges (*cf.* ref. 4), would be rather similar to that of hydroxide ions, and so replacement of water by Me₂SO would not be expected to increase the ionization of silanols by a large amount.

In MeOH, there is a factor of 9 between the rate constants for cleavage of PhCH₂SiMe₂OMe and PhCH₂SiMe₃. If we assume a factor of 10 between the rate constants for the simple bimolecular cleavage of PhCH₂SiMe₂OH and PhCH₂SiMe₃ in Me₂SO-H₂O, then from the slope, 7 × 10⁻⁴ s⁻¹ of the plot of *k*_{obs} against *r*, and the value of *K* of 13 dm³ mol⁻¹, a value of 6.2 × 10⁻⁴ s⁻¹ can be derived for *k*_{AO⁻}. Similarly for the 3:1 medium, use of a value of *k*_{AOH} of 4.0 dm³ mol⁻¹ s⁻¹ for bimolecular cleavage of PhCH₂SiMe₂OH along with one of 200 dm³ mol⁻¹ for *K*, leads to a value of 6.5 × 10⁻³ s⁻¹ for *k*_{AO⁻}. (A factor of 10 between the rate constants for the unimolecular process in the two media is reasonable, since the silanolate ion would be stabilized by hydration more effectively in the more aqueous medium than in the less; but there would be significantly less difference between the effects of hydration on

Table 1. First-order rate constants *k* for cleavage of XC₆H₄CH₂SiMe₃ in *x*:1 v/v Me₂SO-H₂O containing MOH (M = K or Na).

θ/°C	<i>x</i>	X = <i>m</i> -Cl ^a			X = H ^b	
		10 ² [MOH]/mol dm ⁻³	10 ² <i>k</i> /s ⁻¹	<i>k</i> /[MOH]	[KOH]/mol dm ⁻³	10 ⁵ <i>k</i> /s ⁻¹
25	3	0.675	0.39	0.58		
		1.50	0.77	0.51		
		2.80	1.38	0.49		
		4.00	1.59	0.42		
		8.13	2.65	0.32		
		9.25	3.19	0.35		
		12.7	3.77	0.30		
		8.05 ^d	3.13 ^d	0.39		
		9.00 ^d	3.45 ^d	0.38		
		11.2 ^d	3.90 ^d	0.35		
50	3			0.200	800	
50	1			0.200	2.00	
25	1	0.725	0.129			
50	1	0.72	0.99			

^a 8 × 10⁻⁴ mol dm⁻³. ^b 15 × 10⁻⁴ mol dm⁻³. ^c M = K unless otherwise indicated. ^d M = Na.

Table 2. First-order rate constants *k*_{obs} for cleavage of 50.0 °C of XC₆H₄SiMe₂OH in *x*:1 v/v Me₂SO-H₂O containing KOH.

X = H ^a				X = <i>m</i> -Cl ^b	
<i>x</i> = 1		<i>x</i> = 3		<i>x</i> = 1	
10 ² [KOH]/mol dm ⁻³	10 ⁵ <i>k</i> _{obs} /s ⁻¹	10 ⁴ [KOH]/mol dm ⁻³	10 ³ <i>k</i> _{obs} /s ⁻¹	10 ² [KOH]/mol dm ⁻³	10 ⁴ <i>k</i> _{obs} /s ⁻¹
0.50	6.0	5.5	0.48	0.100	2.5
3.00	24.8	24	2.52	0.50	6.0
5.00	31.5	60	4.65	1.00	11.0
10.0	38.5	140	6.2	3.00	26.0
20.0	49	340	7.5	5.00	38.0
42.0	56.5	1 020	8.0	10.0	51
60	62	2 100	8.2	20.0	57.5
84	66			42	67
				59	68
				84	71

^a 1.45 × 10⁻³ mol dm⁻³. ^b 1.6 × 10⁻³ mol dm⁻³.

Table 3. First-order rate constants k_{obs} for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ (8.0×10^{-4} mol dm $^{-3}$) in $x:1$ v/v Me $_2\text{SO-H}_2\text{O}$ containing KOH.

$x = 1; \theta = 25^\circ\text{C}$		$x = 1; \theta = 50^\circ\text{C}$		$x = 3; \theta = 25^\circ\text{C}$	
$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
2.25	0.137	25.0	2.93	2.20	4.6
16.5	0.67	45.0	3.00	7.50	5.7
27.0	0.176	48.0	3.30	10.0	5.6
49.0	0.188	97	3.45	10.0	5.8 ^a
105	0.212	135	3.70	12.5	5.5
150	0.213	200	3.70	24.0	4.9
195	0.213	320	4.45	35.0	4.25
280	0.230	610	4.5	60	3.9
280 ^b	0.221 ^b	1 350	5.2	70	3.8
440	0.231			120	3.9
500	0.240			145	3.2
600	0.224			16.3	3.5

^a This run was carried out with a different batch of Me $_2\text{SO}$ in order to check on reproducibility. ^b Initial concentration of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ was 4.0×10^{-4} mol dm $^{-3}$.

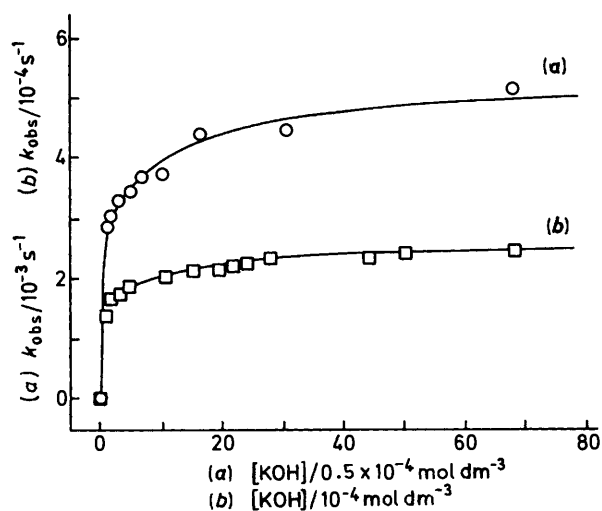


Figure 1. Plot of k_{obs} against concentration of KOH for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ in 1:1 v/v Me $_2\text{SO-H}_2\text{O}$ at 50 °C [curve (a)] and 25 °C [curve (b)]. The lines shown are those generated from equation (5) by use of the values of K_1 , K_2 , B , and $k_{\text{A}(\text{O}^-)_2}$ shown in Table 4.

the transition states, with their dispersed negative charges.) In terms of this analysis, the unimolecular process would contribute *ca.* 90% of the value of k_{obs} in the 1:1 medium and *ca.* 80% in the 3:1 medium.

We must, however, consider the possibility that the cleavage of $\text{PhCH}_2\text{SiMe}_2\text{O}^-$ makes no contribution in either medium. In this case, for the 1:1 medium, from the value of k_{obs} of 3.5×10^{-4} s $^{-1}$ at r 0.50 and $[\text{OH}]^-$ 0.075 mol dm $^{-3}$, it would follow from equation (1) that k_{AOH} 9.3×10^{-3} dm 3 mol $^{-1}$ s $^{-1}$. A similar calculation for the 3:1 medium gives k_{AOH} 1.7 dm 3 mol $^{-1}$ s $^{-1}$. The results imply an increase in k_{AH} on going from the 1:1 to the 1:3 medium by a factor of only 180, compared with that

* In the subsequent discussion we assume that no significant amounts of siloxane species are present in the very dilute solutions of the diol (or later a triol) used. (In keeping with this assumption a doubling of the initial concentration of the diol had no significant effect on the observed rate constant.) Powerful support for the assumption comes from the observation that only mononuclear species are present in solutions of $\text{Si}(\text{OH})_4$ in aqueous alkali, and that in concentrated solutions of alkali only $\text{Si}(\text{OH})_2(\text{O}^-)_2$ is present.⁷

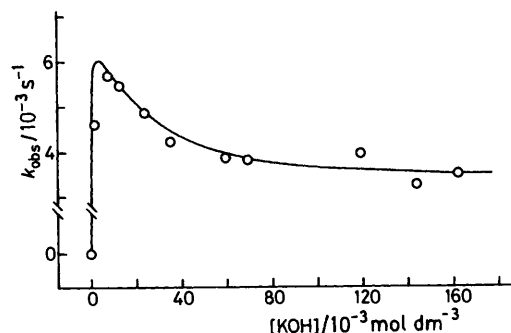


Figure 2. Plot of k_{obs} against concentration of KOH for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ in 3:1 v/v Me $_2\text{SO-H}_2\text{O}$ at 25 °C. The line shown is that generated from equation (5) by use of the values of K_1 , K_2 , B , and $k_{\text{A}(\text{O}^-)_2}$ shown in Table 4.

of *ca.* 400 observed for $\text{PhCH}_2\text{SiMe}_3$. They also imply that the value of the second-order rate constant for $\text{PhCH}_2\text{SiMe}_2\text{OH}$ would be 93 times as large as that for $\text{PhCH}_2\text{SiMe}_3$ in the 1:1 and 40 times in the 3:1 medium. These factors seem rather large, but are not so improbable as to rule out completely the possibility that cleavage of the anion makes no significant contribution in either medium. We suspect that there is, indeed, a contribution from this process, but that it is perhaps not as dominant as was suggested on the basis of our assumption that the bimolecular cleavage of $\text{PhCH}_2\text{SiMe}_2\text{OH}$ is only ten times as fast as that of $\text{PhCH}_2\text{SiMe}_3$.

We also examined the cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{OH}$ (generated *in situ* from $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{OMe}$) in 1:1 Me $_2\text{SO-H}_2\text{O}$ at 50 °C, with the results shown in Table 2. The data can be best fitted (and the fit is very good) for a value of K of 20 cm 3 mol $^{-1}$, and such a value, *ca.* 50% larger than that determined for $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_2\text{OH}$, is reasonable in view of the increase in acidity associated with the electron withdrawal by the *m*-Cl substituent. The corresponding limiting rate constant at high base concentrations is calculated as 7.7×10^{-3} s $^{-1}$, *ca.* 110 times larger than that for $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_2\text{OH}$. (Both k_{AOH} and k_{AO^-} would be expected to be substantially larger for the *m*-chloro compound.)

We then turned to cleavage in 1:1 and 3:1 Me $_2\text{SO-H}_2\text{O}$ of the diol $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})_2$ [subsequently often denoted by $\text{RSiMe}(\text{OH})_2$ or $\text{A}(\text{OH})_2$], generated *in situ* from $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OMe})_2$.* The values of the rate constants are shown in Table 3, and plots of k_{obs} against $[\text{OH}^-]$ appear in Figures 1 and 2.

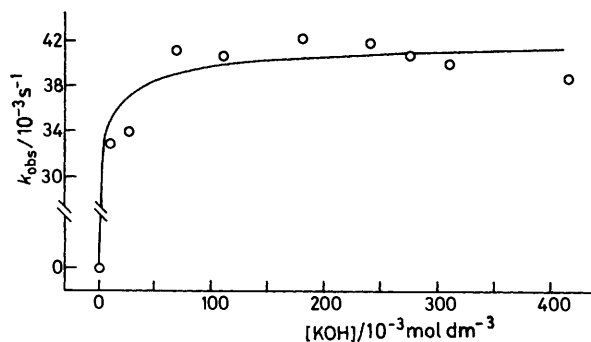
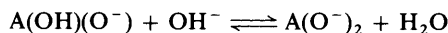
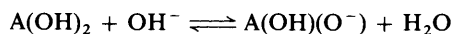


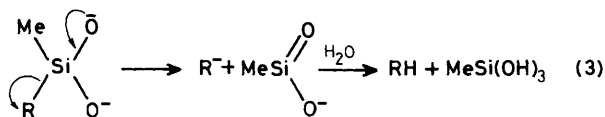
Figure 3. Plot of k_{obs} against concentration of KOH for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si(OH)}_3$ in 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$ at 50 °C. The line shown is that derived from equation (5) with the values of K_1 , K_2 , B , and $k_{\text{A(O}^-)_2}$ shown in Table 4.

In solutions of the diol A(OH)_2 the following equilibria will be rapidly established:

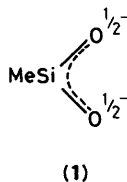


That the second ionization, to give $\text{A(O}^-)_2$, would be likely to be significant was suggested by the fact that the second dissociation constant for orthosilicic acid, Si(OH)_4 , is only *ca.* 100 times smaller than the first, and that in more concentrated aqueous alkali there is virtually complete conversion into $\text{Si(OH)}_2(\text{O}^-)_2$.⁷ A similar difference between the first and second dissociation constants of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe(OH)}_2$, A(OH)_2 , can be confidently expected, and so virtually complete conversion into the dianions $\text{A(O}^-)_2$ in the very strongly basic solutions in the $\text{Me}_2\text{SO-H}_2\text{O}$ media used in the present studies.

It can safely be assumed that the bimolecular cleavage of the doubly charged species $\text{A(O}^-)_2$ by attack of OH^- at silicon is negligibly slow (and, in any case, the dependence of k_{obs} on the base concentration is inconsistent with contributions from such a process), but there is the possibility of unimolecular cleavage, analogous to that recognized for RSiMe_2O^- species, as depicted in equation (3). This process is especially attractive



because the methylsilanolate anion $\text{MeSi(O}^-)=\text{O}$ formed by departure of R^- could be expected to be stabilized in the same way as a carboxylate ion (though to a markedly smaller extent), *i.e.* by the delocalization of the negative charge as in (1). (There is *i.r.* spectroscopic evidence for the existence of silanoic acid in an argon matrix.⁸)



If this picture is correct, then in appropriate regions of base concentration, and provided that this concentration is much greater than that of A(OH)_2 , there should be three cleavage processes contributing to the observed overall rate

constant k_{obs} , which will be given by equation (4). By using the definitions, shown below, of the equilibrium constants K_1 and K_2 for the first and second ionizations of A(OH)_2 , we can convert equation (4) into (5) where $K_1 = [\text{A(OH)(O}^-)]/[\text{OH}^-][\text{A(OH)}_2]$, $K_2 = [\text{A(O}^-)_2]/[\text{OH}^-][\text{A(OH)(O}^-)]$, and $B = (k_{\text{A(OH)}_2}/K_1K_1) + (k_{\text{A(OH)(O}^-)}/K_2)$.

$$k_{\text{obs}} = k_{\text{A(OH)}_2}[\text{A(OH)}_2][\text{OH}^-] + k_{\text{A(OH)(O}^-)}[\text{A(OH)(O}^-)] + k_{\text{A(O}^-)_2}[\text{A(O}^-)_2] \quad (4)$$

$$k_{\text{obs}} = \left\{ \frac{B}{[\text{OH}^-]} + k_{\text{A(O}^-)_2} \right\} \frac{K_1K_2[\text{OH}^-]^2}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2} \quad (5)$$

It is important to appreciate that in the region where most of the A(OH)_2 is converted into $\text{A(O}^-)_2$, the concentration of the dianion will be dependent on the square of the base concentration while the equilibrium between A(OH)_2 and $\text{A(OH)(O}^-)$ involves the first power of that concentration. Thus when much of the substrate, say 90%, is present as the dianion, doubling of the base concentration will reduce the concentration of A(OH)_2 by a factor approaching four and that of $[\text{A(OH)(O}^-)]$ by a factor approaching two. At the same time the rate of cleavage of the remaining A(OH)_2 should be doubled, but this will still mean that the contribution from this cleavage will be halved, as will that from the unimolecular cleavage of $\text{A(OH)(O}^-)$. Thus at the higher base concentrations the contributions from the cleavages of A(OH)_2 and $\text{A(OH)(O}^-)$ will fall off rapidly with increasing base concentration, and in the limit the observed rate constant will be that for the unimolecular cleavage of $\text{A(O}^-)_2$. It can thus be seen that as the base concentration is raised from zero there should be an initial steep rise in k_{obs} as the rate of bimolecular cleavage of the A(OH)_2 species rises in line with the base concentration, but then the plot of k_{obs} against $[\text{OH}^-]$ should begin to curve off (as in the cleavage of RSiMe_2OH species) as the monoanion $\text{A(OH)(O}^-)$ is formed. As the base concentration is increased further and significant amounts of the dianion $\text{A(O}^-)_2$ are formed, then if the dianion were unreactive k_{obs} would begin to fall off sharply, ultimately falling effectively to zero, which is not what is observed. If, however, the dianion undergoes cleavage at a significant rate, then the value of k_{obs} might, if that rate were particularly high, level off to a plateau, but it could also pass through a maximum and subsequently level off at a constant value corresponding to the rate constant for the unimolecular cleavage of the dianion alone.

In our view the observed shapes of the plots (Figures 1 and 2) of k_{obs} against $[\text{OH}^-]$ for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-SiMe(OH)}_2$ in 1:1 and 3:1 *v/v* $\text{Me}_2\text{SO-H}_2\text{O}$ must mean that the dianionic species undergoes spontaneous cleavage at a substantial rate. It is important to note that this conclusion remains valid irrespective of the limitations of the rough quantitative analysis which follows.

Equation (5) can be seen to contain four parameters K_1 , K_2 , B , and $k_{\text{A(O}^-)_2}$, and in order to show that the form of the observed plots of k_{obs} against $[\text{OH}^-]$ can be accounted for in a rough quantitative way in terms of our mechanistic assumptions we need to make estimates of K_1 and K_2 in the various media. As noted previously, approximate values for K_1 of 13 and 200 were determined for $\text{PhCH}_2\text{SiMe}_2\text{OH}$ in 1:1 and 3:1 $\text{Me}_2\text{SO-H}_2\text{O}$, respectively, and the corresponding values for $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2(\text{OH})$ can be assumed to be somewhat larger, say 20 (see earlier) and 400. Data for solutions in MeOH (see later) indicates that K_1 for $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe(OH)}_2$ is *ca.* 13 times as large as that for $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{OH}$ in that solvent, and use of this factor for the $\text{Me}_2\text{SO-H}_2\text{O}$ media implies rough values of 300 and 5 000 $\text{dm}^3 \text{mol}^{-1}$ for K_1 in the

Table 4. Values of the quantities $k_{A(O^-)_2}$, $k_{A(OH)(O^-)_2}$, K_1 , K_2 , and B in equation (5), derived as described in the text.

Substrate	Medium	$\theta/^\circ\text{C}$	$10^4 k_{A(O^-)_2}^a$	K_1^b	K_2^b	$10^5 B^c$
$m\text{-ClC}_6\text{H}_4\text{SiMe}(\text{OH})_2$	3:1 Me ₂ SO-H ₂ O	25	30	5 000	50	14
	1:1 Me ₂ SO-H ₂ O	25	2.7	400	4	4.5
	1:1 Me ₂ SO-H ₂ O	50	55	400	4	69
$m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$	19:1 MeOH-H ₂ O	50	1.9	30	0.3	19.5
	3:1 Me ₂ SO-H ₂ O	25	6.7	20 000	200	4.0
	3:1 Me ₂ SO-H ₂ O	50	80	20 000	200	2.5
	1:1 Me ₂ SO-H ₂ O	50	4.2	2 000	18	2.0

^a In s⁻¹; $k_{A(OH)(O^-)_2}$ in the case of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$. ^b In dm³ mol⁻¹. ^c In mol dm³ s⁻¹.

Table 5. First-order rate constants k_{obs} for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$ (8.0×10^{-4} mol dm⁻³) in $x:1$ Me₂SO-H₂O containing KOH.

$x = 1; \theta = 50^\circ\text{C}$		$x = 3; \theta = 50^\circ\text{C}$		$x = 3; \theta = 25^\circ\text{C}$	
$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3[\text{KOH}]/\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
11.0	.33	1.0	4.0	1.00	1.26
27.5	0.34	5.0	12.2	3.60	1.74
68	0.41	8.0	15.5	11.0	1.75
110	0.41	13.5	15.5	36.5	1.56
180	0.42	22.0	13.9	55	1.25
240	0.42	27.5	14.1	60	1.27
275	0.41	36.0	13.2	74.5	1.06
305	0.40	41.5	13.1	89	0.98
415	0.39	56.5	12.8	118	0.91
		61	11.8	131	0.86
		71	11.3		
		79	11.0		
		104	9.8		
		115	9.2		
		139	8.7		
		145	8.3		

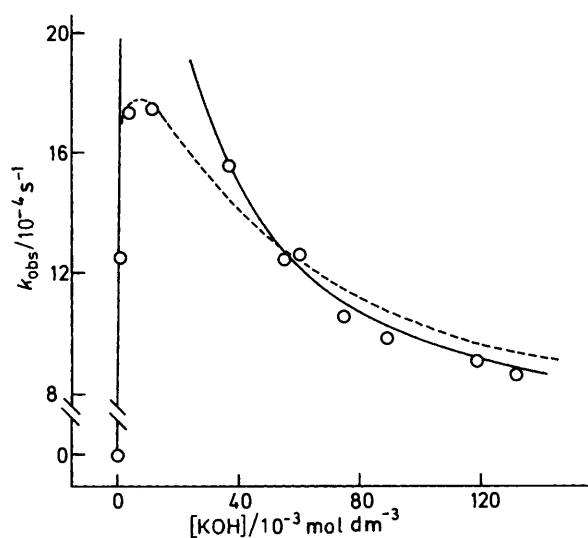


Figure 4. Plot of k_{obs} against concentration of KOH for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$ in 3:1 v/v Me₂SO-H₂O at 25 °C. The solid line shown is that derived from equation (5) by use of the values of K_1 , K_2 , B , and $k_{A(O^-)_2}$ shown in Table 4, and the dotted line is derived similarly but with K_2 1 000 dm³ mol⁻¹, K_2 20 dm³ mol⁻¹, $10^5 B$ 11 mol dm⁻³ s⁻¹, and $k_{A(O^-)_2} = 45 \times 10^{-5}$ s⁻¹.

1:1 and 3:1 media, respectively. (In the actual simulations a value of 400 dm³ mol⁻¹ was used for the 1:1 medium). We then assume that K_2 is smaller than K_1 by a factor of ca. 10², which is the ratio between the first and second ionization constants of Si(OH)₄.⁷ An approximate value of $k_{A(O^-)_2}$ is then estimated from the value of k_{obs} in the roughly level portion of the plot of

k_{obs} against $[\text{OH}^-]$, and a computer analysis used to give a rough value for B . The analysis is then carried on to give the best-fit values of $k_{A(O^-)_2}$ and B , with the results shown in Table 4. In Figures 2 and 3 the lines shown are those calculated by use of the relevant values of K_1 , K_2 , B , and $k_{A(O^-)_2}$ shown in Table 4, and it will be seen that for both media the observed form of the variation of k_{obs} with $[\text{OH}^-]$ is reasonably reproduced. That the value B is ca. 30 times as large for the 3:1 as for the 1:1 medium reflects the fact that the value of the rate constant $k_{A(OH)_2}$ is raised much more than the values of the equilibrium constants K_1 and K_2 by the change from the more to the less aqueous medium.

It can be seen from Table 4 (or, indeed, simply from the values of k_{obs} at the highest base concentrations in the two media) that the value of $k_{A(O^-)_2}$ in the 3:1 is ca. 10 times as large as that in the 1:1 medium at 25 °C. Such a factor is consistent with the less effective hydration of the A(O⁻)₂ ion in the former than in the latter medium, as discussed for the PhCH₂SiMe₂O⁻ anion earlier.

We note at this point that the form of the dependence of k_{obs} on the base concentration is consistent not only with the assumed unimolecular dissociation of the $m\text{-ClC}_6\text{H}_4\text{SiMe}(\text{O}^-)_2$ anion but also with a rate-determining bimolecular reaction between OH⁻ and $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{OH})(\text{O}^-)$. In the latter case, however, the attack of the hydroxide on the silicon atom bearing a negatively charged oxygen atom would have to occur about as readily as that on the silicon atom in the uncharged $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$, which seems highly unlikely. From the values of $k_{A(O^-)_2}$ derived for $m\text{-ClC}_6\text{H}_4\text{SiMe}(\text{OH})_2$ in the 1:1 medium at 25 and 50 °C, rough values of the activation parameters can be derived, viz. ΔH^\ddagger 22.5 kcal mol⁻¹ and ΔS^\ddagger 0.5 cal mol⁻¹ K⁻¹. Such values, especially the near zero entropy of activation, are consistent with a unimolecular process, and

Table 6. First-order rate constants k for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-SiMe}(\text{OX})_2$ ($\text{X} = \text{H}$ or Me)^a at 50 °C in 19:1 v/v $\text{MeOH-H}_2\text{O}$ containing NaOX.

$10^3[\text{NaOX}]/\text{mol dm}^{-3}$	$10^5 k/\text{s}^{-1}$	$10^3[\text{NaOX}]/\text{mol dm}^{-3}$	$10^5 k/\text{s}^{-1}$
30.0	2.37	570	7.4
45.0	3.80	870	8.15
180	5.1	930	8.5
265	5.9	1 640	10.3
380	6.95	3 000	11.6

^a Solution made up to contain $1.3 \times 10^{-3} \text{ mol dm}^{-3} m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-SiMe}(\text{OMe})_2$.

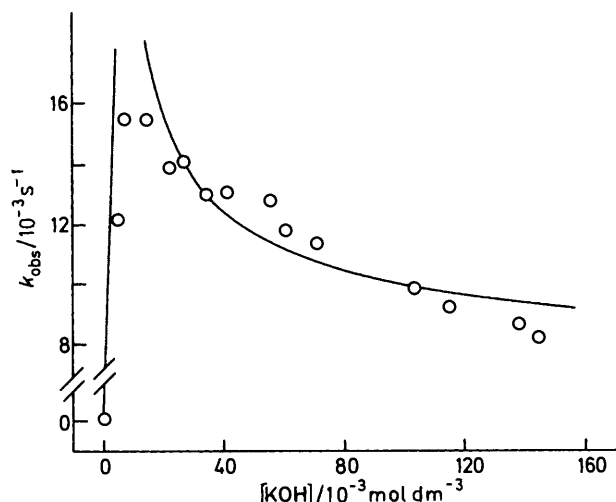


Figure 5. Plot of k_{obs} against concentration of KOH for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Si}(\text{OH})_3$ in 3:1 v/v $\text{Me}_2\text{SO-H}_2\text{O}$ at 50 °C. The line shown is that derived from equation (5) with the values of K_1 , K_2 , and $k_{\text{A}(\text{O}^-)_2}$ shown in Table 4.

although they are subject to considerable error the differences from the values noted earlier for cleavage of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-SiMe}_3$ by a bimolecular mechanism in this medium, *viz.* ΔH^\ddagger 15.0 kcal mol⁻¹ and ΔS^\ddagger -22 cal mol⁻¹ K⁻¹, are probably significant.

We also examined the cleavage of the triol $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-Si}(\text{OH})_3$, $\text{A}(\text{OH})_3$, in the $\text{Me}_2\text{SO-H}_2\text{O}$ media, with the results shown in Table 5 and Figures 3 and 4. The forms of the plots k_{obs} against $[\text{OH}^-]$ are generally similar to those for the $\text{A}(\text{OH})_2$ system. We assume that only the ionizations to $\text{A}'(\text{OH})_2(\text{O}^-)$ and $\text{A}'(\text{OH})(\text{O}^-)_2$ are important, since no formation of $\text{Si}(\text{OH})(\text{O}^-)_3$ is observed in strongly basic aqueous solutions of $\text{Si}(\text{OH})_4$.⁷ [Even if some $\text{A}'(\text{O}^-)_3$ were formed this should have a fairly small effect on k_{obs} since the trianion could be expected to undergo unimolecular cleavage at a rate comparable to that for $\text{A}'(\text{OH})(\text{O}^-)_2$.]

We assume that, because of the electron withdrawal by the additional OH group, the values of K_1 and K_2 [as defined for $\text{A}(\text{OH})_2$] will be somewhat larger, say by a factor of 4-5, than those for $m\text{-ClC}_6\text{H}_4\text{SiMe}(\text{OH})_2$. The line shown in Figure 4 for cleavage in 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$ at 50 °C is based on values of K_1 and K_2 of 2 000 and 18 dm³ mol⁻¹, respectively [giving B $2 \times 10^{-5} \text{ mol dm}^{-3}$ and $k_{\text{A}'(\text{OH})(\text{O}^-)}$ $4.2 \times 10^{-4} \text{ s}^{-1}$]. For the 3:1 medium values of K_1 and K_2 of 20 000 and 200 dm³ mol⁻¹ were used, and it will be seen that the fit is poor in the region of very low base concentrations, where the condition $[\text{A}'(\text{OH})_3] \ll [\text{OH}^-]$ is not met, but good in the later portion. [A much better

fit, reproducing the observed maximum in k_{obs} , is obtained if values of K_1 and K_2 of 1 000 and 20 respectively, are used (see dotted line in Figure 4), and in view of the many assumptions made these values cannot be regarded as wholly unrealistic.]

The rate constant for the decomposition of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-Si}(\text{OH})(\text{O}^-)_2$ would not be expected to be much different from that for $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}(\text{O}^-)_2$; in fact, the derived value of $k_{\text{A}'(\text{OH})(\text{O}^-)_2}$ is apparently roughly four times as large as that of $k_{\text{A}(\text{O}^-)_2}$ in the 3:1 medium at 25 °C, and the corresponding factor is *ca.* 13 in the 1:1 medium at 50 °C.

We also examined the cleavage at 50 °C of $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-SiMe}(\text{OH})_2$ in 19:1 v/v $\text{MeOH-H}_2\text{O}$ containing NaOH, with the results shown in Table 6. The plot (see Figure 5) of k_{obs} against $[\text{OH}^-]$ (the presence of some methoxide ion being neglected for simplicity) was of the same form as that for the reaction in 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$, but, of course, much higher base concentrations had to be used in the methanolic medium. Use of a value of 30 dm³ mol⁻¹ for K_1 , and so one of 0.3 dm³ mol⁻¹ for K_2 , gave a good fit to the experimental data with $k_{\text{A}(\text{O}^-)_2}$ $1.9 \times 10^{-4} \text{ s}^{-1}$; this value is *ca.* 30 times smaller than that in 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$, a factor reasonably in line with that of 13 between the values in 3:1 and 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$, and attributable to the more effective solvation of the dianion in the aqueous-methanolic medium. The important feature is that the absence of a fall-off in the k_{obs} at the high base concentrations means that the dianion is undergoing unimolecular cleavage [of the type shown in reaction (3)], and this provides strong support for our view that the monoanion also undergoes such cleavage in the $\text{MeOH-H}_2\text{O}$ medium.

The unsaturated intermediate formed from $\text{RSi}(\text{OH})(\text{O}^-)_2$, $\text{HO}(\text{O}^-)\text{Si}=\text{O}$, is, of course, the anion of the hypothetical metasilicic acid, and the species formed from the dianions $\text{RSiMe}(\text{O}^-)_2$ can also be regarded as derived from that acid, or from the hypothetical metasilicous acid, $\text{H}(\text{HO})\text{Si}=\text{O}$.

Experimental

Materials.—Methanol was dried as described previously.⁹ Dimethyl sulphoxide was boiled with CaH_2 for 10 h then distilled under reduced pressure. Compounds $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{-Me}_n(\text{OMe})_{3-n}$ ($n = 0-2$) were made as previously described.⁹

Rate Measurements.—Rates were measured spectrophotometrically as previously described.^{1b} The wavelengths (in nm) were: (a) for $\text{PhCH}_2\text{SiMe}_3$, 275.6; (b) for $\text{PhCH}_2\text{SiMe}_2\text{OMe}$ and $m\text{-ClC}_6\text{H}_4\text{SiMe}_2\text{OH}$, 279; (c) for $m\text{-ClC}_6\text{H}_4\text{SiMeOH}_2$, 278 in $\text{Me}_2\text{SO-H}_2\text{O}$ and 282 in $\text{MeOH-H}_2\text{O}$; and (d) for $m\text{-ClC}_6\text{H}_4\text{Si}(\text{OH})_3$, 277.

A stock solution, *ca.* 1-2 mmol dm⁻³ of the relevant organosilicon compound in the $\text{Me}_2\text{SO-H}_2\text{O}$ medium was prepared *ca.* 24 h before use. (There was no effect on k_{obs} when the solution was used 5 h or 3 days after being made up.) A suitable volume of the stock solution, pre-warmed to the reaction temperature, was taken, and the reaction started by addition from a microsyringe of an appropriate volume of 2.0 mol dm⁻³ KOH in 1:1 $\text{Me}_2\text{SO-H}_2\text{O}$ or 0.28 mol dm⁻³ KOH in 3:1 $\text{Me}_2\text{SO-H}_2\text{O}$, these solutions also being pre-warmed. Solutions in $\text{MeOH-H}_2\text{O}$ were made up as previously described.⁸ Good first-order kinetics were observed within a run, and the rate constants for $\text{PhCH}_2\text{SiMe}_3$ and the $\text{PhSiCH}_2\text{SiMe}_n(\text{OMe})_{3-n}$ compounds were reproducible to within *ca.* 3% for reactions in 1:1 and $\pm 6\%$ for those in 3:1 $\text{Me}_2\text{SO-H}_2\text{O}$, but reproducibility was somewhat poorer in the case of $m\text{-ClC}_6\text{H}_4\text{Si}(\text{OH})_3$.

Determination of K for $\text{PhCH}_2\text{SiMe}_2\text{OH}$.—Solutions ($1.45 \times 10^{-3} \text{ mol dm}^{-3}$) of $\text{PhCH}_2\text{SiMe}_2\text{OH}$ (from $\text{PhCH}_2\text{SiMe}_2\text{OMe}$) in $\text{Me}_2\text{SO-H}_2\text{O}$ containing base were made up as

described for the rate studies, but at room temperature. The optical density at 279.3 nm of each solution was recorded quickly, and the values (with molarities of base in parentheses were): 0.0135 (0.00), 0.21 (5.5×10^{-4}), 0.43 (2.4×10^{-3}), 0.70 (6.0×10^{-3}), 0.89 (1.4×10^{-2}), 1.03 (3.4×10^{-2}), 1.11 (1.02×10^{-1}), and 1.14 (2.1×10^{-1}). From a plot of optical density against the base concentration it was judged that the conversion into the dianion was half complete in *ca.* $0.005 \text{ mol dm}^{-3}$ base, which implies a value of *K* of $200 \text{ dm}^3 \text{ mol}^{-1}$.

A similar procedure for the 1:1 medium gave optical densities at specified base concentrations as follows: 0.00 (0.000), 0.02 (0.0025), 0.05 (0.005), 0.21 (0.025), 0.33 (0.05), 0.465 (0.10), 0.58 (0.20), 0.66 (0.60), 0.74 (0.84). It was judged that conversion into the dianion was half complete in *ca.* $0.075 \text{ mol dm}^{-3}$ base, which implies a value of *K* of $13 \text{ dm}^3 \text{ mol}^{-1}$.

Acknowledgements

We thank Dr. M. Cypryk for invaluable help with the computer analyses, the Polish Academy of Sciences for support within Problem CPBP 01.13, and the SERC for support to C. E.

References

- 1 (a) Z. H. Aiube, J. Chojnowski, C. Eaborn, and W. A. Stańczyk, *J. Chem. Soc., Chem. Commun.*, 1983, 493; (b) C. Eaborn and W. A. Stańczyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2099.
- 2 Z. H. Aiube, D.Phil. Thesis, University of Sussex, 1984.
- 3 J. Chmielecka, J. Chojnowski, C. Eaborn, and W. A. Stańczyk, *J. Chem. Soc., Chem. Commun.*, 1987, 1337.
- 4 J. R. Jones, 'The Ionization of Carbon Acids,' Academic Press, London, 1973, pp. 102–105.
- 5 D. Dolman and R. Stewart, *Can. J. Chem.*, 1967, **45**, 911.
- 6 C. Eaborn, J. R. Jones, and G. Seconi, *J. Organomet. Chem.*, 1976, **116**, 83.
- 7 N. Ingri, in 'Aqueous Silicic Acid, Silicates, and Silicate Complexes in Biochemistry of Silicon and Related Problems,' eds. S. Bendz and I. Lindquist, Plenum Press, New York, 1978, pp. 3–51.
- 8 R. Withall and L. Andrews, *J. Am. Chem. Soc.*, 1985, **107**, 2567.
- 9 J. Chmielecka, J. Chojnowski, C. Eaborn, and W. A. Stańczyk, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1779.

Received 13th June 1988; Paper 8/02349B