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POLAR EFFECTS ON THE ACID AND BASE CATALYSED CLEAVAGE OF BENZYLOXYSILANES

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Summary

The compounds $(XC_6H_4)Me_2SiOCH_2C_6H_4Y$ have been cleaved in absolute ethanol containing chloroacetic acid or sodium ethoxide. In the specific acid catalysed solvolysis the Hammett ρ-values are: $\rho_{Si} = -0.55$ and $\rho_Y = -0.54$. In the first-order base catalysed solvolysis the corresponding values are: $\rho_{Si} = 1.5$ and $\rho_Y = 1.1$. Activation entropies are —46 and —50 cal mol^{-1} K^{-1} in the acid and base catalysed reactions, respectively, with corresponding activation enthalpies of 9 and 7 kcal mol^{-1}. The different sensitivities to polar effects in acid and base catalysed reactions are discussed in terms of solvation of the transition states.

Introduction

Solvolysis of R_3SiY compounds have usually been discussed in terms of bimolecular mechanisms, which may be of the synchronous type, or may involve addition complexes. Reaction mechanisms have been studied by both kinetic and non-kinetic methods, and some of the main results have been reviewed recently [1].

In the present work rates for acid and base catalysed ethanolysis of benzyloxysilanes of the general type $(XC_6H_4)Me_2SiOCH_2C_6H_4Y$ are studied as a function of substituents on both sides of the bond being broken, and the results are analysed by means of the Hammett equation.

Ethanolysis of phenoxysilanes was assigned a S_N2—*Si* mechanism in the acid catalysed process, while pentacoordinate complexes could not be excluded for the acid catalysed reaction [2]. A similar pattern is found for the benzyloxysilanes.

Results and discussion

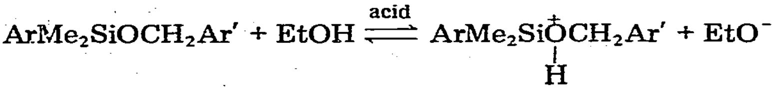
Benzyloxysilanes react in absolute ethanol containing acid or base according to eq. 1. The reaction is first-order with respect to the organosilicon compound.

$$\mathrm{(XC_6H_4)Me_2SiOCH_2C_6H_4Y + EtOH \rightarrow (XC_6H_4)Me_2SiOEt + HOCH_2C_6H_4Y} \quad (1)$$

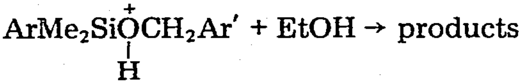
Acid-catalysed solvolysis

The reaction rates in absolute ethanol containing chloroacetic acid buffers are independent of the acid concentration at a fixed buffer ratio, and the reaction is therefore specific acid catalysed (see Table 1). This is the first example of specific acid catalysed solvolysis of R_3SiOC compounds, but such catalysis has been found in the cleavage of *N*-silyl substituted anilines [3].

The protonation of the substrate takes place in a rapid preequilibrium step, corresponding to eq. 2.



$$\mathrm{ArMe_2SiOCH_2Ar' + EtOH \overset{acid}{\rightleftharpoons} ArMe_2Si\underset{H}{\overset{+}{O}}CH_2Ar' + EtO^-} \quad (2a)$$



$$\mathrm{ArMe_2Si\underset{H}{\overset{+}{O}}CH_2Ar' + EtOH \rightarrow products} \quad (2b)$$

The proton is shown attached to the oxygen atom by analogy with the behaviour of alkoxysilanes in strongly acidic solution [4].

In step 2b the Si—benzyloxy bond is broken and a new Si—O bond is formed. Depending on the relative importance of associative and dissociative processes various differential charges will develop on the silicon atom and on the leaving group in the transition state.

The ρ-values given in Tables 1 and 2 demonstrate that there are positive charges on both sides of the bond being broken. In terms of a synchronous mechanism the ρ_{Si}-value indicates that the Si—benzyloxy bond is broken to a slightly greater extent than the new Si—O bond is formed. From the ρ_Y-value, and assuming a normal transmission coefficient for the methylene group of 0.4 [5] it is seen that there is a substantial positive charge on the oxygen atom of

TABLE 1

SOLVOLYSIS OF $(XC_6H_4)Me_2SiOCH_2Ph$ IN ABSOLUTE ETHANOL CONTAINING CHLOROACETIC ACID BUFFERS
AT 25.0°C, EXCEPT WHEN GIVEN IN PARENTHESES (45.0°C)[a,b,c]

	$k \times 10^4$ (sec^{-1})			$\bar{k}$
$ClCH_2COOH$ (*M*)	0.0417	0.0227	0.0119	
NaOEt (*M*)	0.00417	0.00227	0.00119	
X				
p-MeO	9.90	9.45	9.70	9.68
p-Me	9.87	9.95	9.74	9.85
m-Me	9.29 (26.1)	9.15 (25.8)	9.20	9.21
H	8.44	8.40	8.30	8.38
p-F	6.55	6.70	6.64	6.63
p-Cl	5.72 (14.6)	5.57 (14.1)	5.53	5.61
m-Cl	5.24	5.16	5.10	5.17

[a] $\rho = -0.55$, standar deviation 0.02, correlation coefficient 0.9953. [b] $\Delta S^{\ddagger} = -46$ cal mol^{-1} K^{-1}, $\Delta H^{\ddagger} = 8.8$ kcal mol^{-1}. [c] $\mu = 0.050$ by addition of $LiClO_4$.

TABLE 2

SOLVOLYSIS OF $Me_2PhSiOCH_2C_6H_4Y$ IN ABSOLUTE ETHANOL CONTAINING CHLOROACETIC ACID BUFFERS AT 25.0°C[a,b,c]

Y	p-MeO	p-Me	m-Me	p-Cl	m-Cl	p-NO$_2$
$k \times 10^4$ (sec^{-1})	9.93	10.4	9.51	5.92	4.83	3.20

[a] $\rho = -0.54$, standard deviation 0.03, correlation coefficient 0.9937. [b] $\mu = 0.050$ by addition of $LiClO_4$. [c] $c\ ClCH_2COOH = 0.0417\ M$, $c\ NaOEt = 0.00417\ M$.

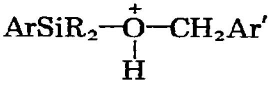
the benzyloxy group in the transition state. The Si—benzyloxy bond therefore cannot be cleaved to any great extent, and overall the transition state is reactant-like.

$[EtOH{-}{-}{-}{-}SiR_3{-}{-}HOCH_2Ar']^+$

(I)

ρ: −0.55 −1.4

For a very reactant-like transition state with the Si—benzyloxy bond only slightly weakened, the positive charge is "symmetrical" with respect to the substituted phenyl groups.



$ArSiR_2{-}\overset{+}{\underset{H}{O}}{-}CH_2Ar'$

(II)

ρ: −0.55 −0.54

Polar effects are transmitted through a silicon atom in a manner similar to that for carbon [6], and the identical ρ_{Si}- and ρ_Y-values are understandable on this basis.

Compared to the cleavage of the silicon—phenoxy bond [2,7] the silicon—benzyloxy bond is less broken in the transition state which is thus reached earlier for the benzyloxysilanes resulting in faster rates. The faster rates are found for the most basic organosilicon substrates, demonstrating the importance of the protonation step 2a, or in other words that k_{rel} is mainly determined by the equilibrium constants for step 2a.

$$k_{rel} = \frac{k_{obs\,1}}{k_{obs\,2}} = \frac{K_1\,(2a)}{K_2\,(2a)} \times \frac{k_1\,(2b)}{k_2\,(2b)} \tag{3}$$

This principle can be extended to other substrates, e.g. silylanilines [8] and silylpyrroles [9], and the following rate sequence is obtained: $R_3SiNMePh > R_3SiOCH_2Ph > R_3SiOPh \simeq R_3SiNC_4H_4$.

The addition—elimination mechanism would have to involve rate determining formation of the pentacoordinate complex III, in order to explain the effect of substituents in the cleaved group on reaction rates.

$[EtOH{-}SiR_3{-}HOCH_2Ar']^+$

(III)

This conclusion is reached also by consideration of relative stabilities of positive charge in the transition states for formation and breakdown of the complex. The transition state for formation of the complex involves a positive charge localised on benzyl alcohol, which is a stronger acid than ethanol [10], and this transition state will be of higher energy than the transition state of breakdown of the complex. With a new bond partly formed between the nucleophile and the silicon atom the positive charge on silicon resulting from inductive transfer from the protonated leaving group will be reduced. A slightly positive silicon atom is not, however, inconsistent with the two-step mechanism, which is an acceptable model for the acid catalysed reaction.

If the two-step mechanism is valid for R_3SiY with $Y = OCH_2Ar'$ and OAr [2], the different ρ_Y-values (and identical ρ_{Si}-values) in the two reaction series must be explained by a different degree of nucleophilic assistance from the solvent in the two cases. The most efficient stabilisation (dispersal) of positive charge is found for the most acidic leaving group.

Base-catalysed solvolysis

Catalysis by base is less efficient than acid catalysis, and the addition of approximately 10^{-3} *M* sodium ethoxide to the absolute ethanol was necessary to give convenient rates of solvolysis. The rates increase linearly with the concentration of added base (see Table 3).

TABLE 3

SOLVOLYSIS OF $(XC_6H_4)Me_2SiOCH_2Ph$ IN ABSOLUTE ETHANOL CONTAINING SODIUM ETHOXIDE AT 25.0°C, EXCEPT WHEN GIVEN IN PARENTHESES (45.0°C)[a,b,c]

X	NaOEt × 10^3 (*M*)	$k \times 10^3$ (sec^{-1})	$k/[NaOEt] = k_B$	$\bar{k}_B$
p-MeO	1.43	1.95	1.36	1.44
	3.60	5.12	1.42	
	5.57	8.64	1.55	
p-Me	1.43	2.22	1.55	1.57
	3.60	5.66	1.57	
	5.57	8.90	1.60	
m-Me	1.43	2.74 (5.49)	1.92 (3.84)	1.92
	3.60	7.08 (13.9)	1.97 (3.86)	
	5.57	10.4	1.87	
H	1.43	3.70	2.59	2.56
	3.60	9.02	2.51	
	5.57	14.4	2.59	
p-F	1.43	6.66	4.66	4.71
	3.60	16.8	4.67	
	5.57	26.7	4.79	
p-Cl	1.43	9.10 (21.0)	6.36 (14.7)	6.45
	3.60	23.0 (55.5)	6.39 (15.4)	
	5.57	36.8	6.61	
m-Cl	1.43	13.2	9.23	9.49
	3.60	34.3	9.52	
	5.57	54.2	9.73	

[a] $\rho = 1.5$, standard deviation 0.02, correlation coefficient 0.9993. [b] $\Delta S^{\ddagger} = -50$ cal mol^{-1} K^{-1}, $\Delta H^{\ddagger} = 6.7$ kcal mol^{-1}. [c] $\mu = 0.050$ by addition of $LiClO_4$.

TABLE 4

SOLVOLYSIS OF $Me_2PhSiOCH_2C_6H_4Y$ IN ABSOLUTE ETHANOL CONTAINING SODIUM ETHOXIDE AT 25.0°C[a,b,c]

Y	*p*-MeO	*p*-Me	*m*-Me	*p*-F	*p*-Cl	*m*-Cl	*p*-NO_2
$k \times 10^3$ (sec^{-1})	2.64	2.60	2.93	5.68	7.21	9.38	28.1

[a] $\rho = 1.1$, standard deviation 0.02, correlation coefficient 0.9991. [b] $\mu = 0.050$ by addition of $LiClO_4$. [c] $[NaOEt] = 1.43 \times 10^{-3}$ *M*.

Electron-attracting substituents on either side of the bond being broken increase the rates and give rise to fairly high ρ-values (Tables 3 and 4). From the ρ_{Si}-value of 1.5 it is concluded that the silicon atom carries a partial negative charge in the transition state as a result of nucleophilic attack by EtO^- (or $EtOH + EtO^-$). The bond formation is thus more advanced than the bond breakage. The rate increasing effect of electron-attracting substituents in the cleaved group suggests that there is a substantial negative charge on the oxygen of the benzyloxy group, and that the breaking of the Si—benzyloxy bond is well advanced in the transition state.

The transition state may be pictured as in IV (*S*$_N$2—*Si*) or V (addition—elimination).

$$[\mathrm{EtO{-}{-}SiR_3{-}{-}{-}OCH_2Ar'}]^- \qquad [\mathrm{EtO{-}SiR_3{-}{-}{-}OCH_2Ar'}]^-$$

(IV) (V)

Structure IV involves a product-like transition state with bond breakage well advanced. Transition state V implies rate determining breakdown of a pentacoordinate silicon complex. However, if one compares the energies of the transition states preceding and following the complex, structure V seems to be open to criticism. It seems reasonable to assume that the transition state for formation of the complex will have a higher energy than the transition state for its breakdown, $^-OCH_2Ar'$ being a weaker base than ^-OEt. The difference in pK_a of the corresponding alcohols is, however, only 0.6 pK_a units [10], and this gives the argument only a suggestive value, and the two-step mechanism cannot be rejected on this basis.

Stereochemical studies, however, support structure IV. Inversion of configuration of R_3SiOMe was found in base catalysed methanolysis [11], and this is the result of the *S*$_N$2—*Si* mechanism, according to the *S*$_N$2—*Si* stereochemistry rule [12,13]. Assuming that R_3SiOCH_2Ar and R_3SiOMe react by a similar mechanism it is reasonable to expect it to be the *S*$_N$2—*Si* mechanism. Thus for the benzyloxysilanes a fairly high ρ_{Si}-value of 1.5 is found in a synchronous reaction. A substantially higher ρ_{Si}-value of 2.8 was found for a leaving group of similar pK_a, viz. the pyrryl anion, and ρ-values of this magnitude probably indicate the existence of pentacoordinate complexes along the reaction coordinate [9].

The benzyloxysilanes react much more slowly than the phenoxysilanes [2], in accord with the lesser degree of stabilisation of negative charge on the leaving group.

Activation entropies

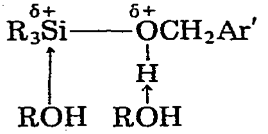
The low activation entropies found in the present study are in line with results for silylacetates [14], phenoxides [15], and 2-sila-1,3-dioxolanes [16]. It was proposed that these highly negative activation entropies result from an expansion of coordination of the silicon atom by use of its *3d* orbitals [15]. Octet expansion is favoured by the presence of two electronegative atoms close to the silicon atom in the transition state. As a result the transition state is more complex for silicon than for carbon. Similar negative activation entropies would then be expected for other substrates containing bonds from silicon to a highly electronegative atom, i.e. Si—N. However, much less negative activation entropies in the range —(10—20) cal mol^{-1} K^{-1} have been found for silylanilines [3] and silylpyrroles [9]. This casts doubt on octet expansion as an explanation for the low activation entropies.

Comparison of acid and base catalysed solvolyses

Rates for the base catalysed reactions are much more sensitive to substituent effects, and the magnitudes of the ρ-values are higher than for the acid catalysed reactions. In the acid catalysed solvolysis the transition state is reactant-like, while base catalysis involves a product-like transition state, as discussed above. The transition states carry formal charges of +1 and —1 units, and this charge is mainly centred on the silicon atom and the leaving group in both cases.

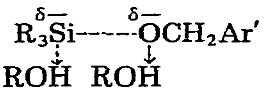
The sums of ρ_{Si}- and ρ_Y-values may therefore be taken as a measure of the total charge on the transition state. For the base catalysed solvolysis $|\rho_{Si} + \rho_Y| = 4.3$ and in the acid catalysed solvolysis $|\rho_{Si} + \rho_Y| = 1.9$. It is therefore concluded that there is less absolute effective charge on the transition state for the acid catalysed solvolysis than for the base catalysed solvolysis.

This difference may be due to better solvation of the acid catalysed transition state; in this case solvation is possible by electron donation from the solvent towards both silicon and oxygen atoms:



$$\begin{array}{ll} \overset{\delta+}{R_3Si}\text{——} & \overset{\delta+}{O}CH_2Ar' \\ \uparrow & | \\ | & H \\ | & \uparrow \\ ROH & ROH \end{array}$$

In the case of the transition state for the base catalysed reaction solvation will involve electron donation towards the solvent molecules:



$$\begin{array}{ll} \overset{\delta-}{R_3Si}\text{----} & \overset{\delta-}{O}CH_2Ar' \\ \downarrow & \downarrow \\ ROH & ROH \end{array}$$

This type of interaction cannot be important for the silicon atom, since electrophilic attack on that atom is highly unfavourable.

It may also be argued that electrophilic stabilisation of the negative leaving group is less efficient than nucleophilic stabilisation of the leaving group in the acid catalysed reaction.

The R_3Si group is classified as a hard electrophilic centre [17], and we may substitute H for R_3Si in the transition state for the acid catalysed reaction which may then be further analysed in terms of relative acid—base strength of solvent and transition state. In the acid catalysed reaction the interaction in the transition state between the leaving group and solvent may be written:

$$H_2\overset{+}{O}CH_2Ar' + EtOH \rightleftharpoons HOCH_2Ar' + Et\overset{+}{O}H_2 \qquad (4)$$

In this equilibrium benzyl alcohol is a weaker base than ethanol [10], and the equilibrium is displaced towards the right. Positive charge is thus removed from the protonated benzyl alcohol, and this corresponds with charge removal from the transition state for the solvolysis, resulting in a smaller absolute ρ-value.

In the base catalysed reaction the solvation of the transition state may be discussed by reference to the equilibrium 5:

$$\bar{O}CH_2Ar' + EtOH \rightleftharpoons HOCH_2Ar' + Et\bar{O} \qquad (5)$$

This equilibrium lies over to the left, since the benzyl alcohol is a stronger acid than ethanol. Removal of charge from the benzyloxy anion is thus not favoured; the negative charge is mainly localised on the oxygen atom resulting in more negative ρ_Y-values.

In the general case of solvolysis of R_3SiY in ROH, for a leaving group YH less basic than ROH, solvation of both leaving group and R_3Si is relatively more efficient in the acid catalysed solvolysis, and $\Sigma|\rho|_{acid} < \Sigma|\rho|_{base}$. For leaving groups YH more basic than ROH, solvation of the leaving group is favoured in the base catalysed reaction, while solvation of R_3Si is favoured in the acid catalysed reaction. As a result, the sums of the absolute ρ-values are more similar for the two types of catalysis. Two reaction series have been described, the results of which are in accord with the present suggestions: For R_3SiOAr the ρ-values are $\Sigma|\rho|_{acid} = 1.1$ and $\Sigma|\rho|_{base} = 1.9$ [2,7], and for $R_3SiNRAr$ $\Sigma|\rho|_{acid} = 3.5$ and $\Sigma|\rho|_{base} = 3.3$ [3,8,18], respectively.

Experimental

Materials

The benzyloxysilanes $(XC_6H_4)Me_2SiOCH_2C_6H_4Y$ were made on a 0.01 *M* scale by the method described for Me_3SiOCH_2Ph [19]. The compounds showed the correct parent peak in the mass spectrum, and had the following boiling points: (°C/mm Hg), Y = H, X = *p*-MeO 180/10, *p*-Me 168/10, *m*-Me 166/10, H 144/10, *p*-F 154/10, *p*-Cl 175/10, *m*-Cl 170/10; X = H, Y = *p*-MeO 194/15, *p*-Me 174/15, *m*-Me 172/15, *p*-F 163/15, *p*-Cl 184/14, *m*-Cl 186/15, *p*-NO_2 226/15. The chlorosilanes necessary for the synthesis of the above compounds were made by the method described in [20].

Reaction products

The reaction of $Me_2PhSiOCH_2Ph$ in absolute ethanol [21] containing acid or base gave two products with retention times identical to those for benzyl alcohol and $Me_2PhSiOEt$ [9]. $XC_6H_4SiOCH_2Ph$ compounds gave products having retention times identical with those for benzyl alcohol and those expected for the $XC_6H_4Me_2SiOEt$ compounds, and $Me_2PhSiOCH_2C_6H_4Y$ gave products identical with those for $HOCH_2C_6H_4Y$ and $Me_2PhSiOEt$.

Rate measurements

The reactions were carried out in absolute ethanol containing acid or base. The ionic strength was adjusted to $\mu = 0.050$ by the appropriate addition of $LiClO_4$. Acidic solutions were made up by adding 25—100 μl of 0.5 *M* chloroacetic acid and an equal amount of 0.05 *M* sodium ethoxide to 1 ml absolute ethanol. Basic solutions consisted of 25—100 μl of 0.05 *M* sodium ethoxide added to 1 ml absolute ethanol. The strength of the sodium ethoxide stock solution was determined by titration. The reaction vessel was kept in a thermostat at 25 or 45 ± 0.1°C. The benzyloxysilane was added by syringe to the reaction solution to give a concentration of about 0.1 *M*, and diphenyltetramethyldisiloxane was added as an internal standard. Samples of 15 μl were withdrawn at regular intervals over a period of two half lives, and the reaction was stopped by injecting into 150 μl absolute ethanol containing 0.01 *M* ammonium acetate. The samples were analysed by GLC on 2 m × 1/8″ columns packed with either 3% SE 30 on 100/120 Versaport 30 for most compounds, or 2% OV-17 on 80/100 Chromosorb W for the compounds with X,Y = H,*p*-F. The decrease in concentration of the benzyloxysilane was followed by measuring peak heights relative to the internal standard which was shown to be unreactive under the experimental conditions chosen. Rate constants were obtained graphically. The solvent used for both acid and base catalysed solvolyses had limited stability, and freshly made solutions had to be used. The rate constant was checked periodically for one of the compounds to exclude the possibility that changes were occurring in the solvent.

References

1 R.H. Prince, in M.L. Tobe (Ed.), MTP Inorg. Chem., Ser. One, Butterworths, London, 1972, Vol. 9, p. 353.
2 B. Bøe, J. Organometal. Chem., 57 (1973) 255.
3 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 25 (1970) 57; 27 (1971) C24.
4 G.A. Olah, D.H. O'Brien and C.Y. Lui, J. Amer. Chem. Soc., 91 (1969) 701.
5 O. Exner, in N.B. Chapman and J. Shorter (Eds.), Advances in Linear Free Energy Relationships, Plenum Press, London—New York, 1972, p. 353.
6 F. Correa-Duran, A.L. Allred, D.E. Glover and D.E. Smith, J. Organometal. Chem., 49 (1973) 353.
7 E. Akerman, Acta Chem. Scand., 11 (1957) 373.
8 B. Bøe, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 82 (1974) 17.
9 B. Bøe, J. Organometal. Chem., 73 (1974) 297.
10 J. Hine and M. Hine, J. Amer. Chem. Soc., 74 (1952) 5266.
11 R. Baker, R.W. Bott, C. Eaborn and P.W. Jones, J. Organometal. Chem., 1 (1963) 37.
12 L.H. Sommer and H. Fujimoto, J. Amer. Chem. Soc., 90 (1968) 982.
13 L.H. Sommer, Stereochemistry, Mechanism and Silicon, Mc Graw—Hill, New York, 1965.
14 R.H. Prince and R.E. Timms, Inorg. Chim. Acta, 1 (1967) 129; 2 (1968) 257, 260.
15 J.R. Chipperfield and G.E. Gould, J. Chem. Soc., Perkin II, (1974) 1324.
16 B. Bøe, J. Organometal. Chem., 43 (1972) 275.
17 R.G. Pearson, in N.B. Chapman and J. Shorter (Eds.), Advances in Linear Free Energy Relationships, Plenum Press, London—New York, 1972, p. 287.
18 M. Ali, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 78 (1974) 83.
19 W. Gerrard and K.D. Kilburn, J. Chem. Soc., (1956) 1536.
20 G. Schott and V. Bondybey, Chem. Ber., 100 (1967) 1773.
21 G. Schott, H. Kelling and R. Schild, Chem. Ber., 99 (1966) 291.