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CLEAVAGE OF α-HALOSUBSTITUTED ALKYL GROUPS FROM SILICON. GENERAL BASE CATALYSIS IN SILICON—CARBON BOND CLEAVAGE

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Summary

A kinetic study has been made of the spontaneous and pyridine-catalysed solvolysis of (trihalomethyl)trimethylsilanes (Me_3SiCX_3, X = Cl, Br) in aqueous n-propanol and aqueous 1,4-dioxane, and of solvolysis of 1-dibromomethyl-1-methylsilacyclobutane in aqueous n-propanol. Possible mechanisms are discussed. A general scheme is proposed for cleavage of Si—C bonds, which involves general base and general base—nucleophile catalysis, in which for one class of reagents viz. (α-haloalkyl)triorganosilanes, all the component reactions have been defined.

Introduction

Previous studies of the base cleavage of α-halosubstituted alkyl groups from silicon focussed our attention on the problems of catalysis in solvolysis involving cleavage of Si—C bonds and we have shown that the removal of α-dihaloalkyl gorups from silicon in the presence of ammonia buffer requires participation of lyate ions [1,2]. Organosilanes having trihalomethyl groups are cleaved much more readily [3], so we expected that extension of our studies to such derivatives would make it possible to study spontaneous solvolysis of Si—C bonds as well as the base-catalysed process.

Results and discussion

General kinetics

The cleavage of (trihalomethyl)trimethylsilanes was too fast in the propanol—water 8 : 2 V/V system in the presence of ammonia buffer, the system used for the dihaloalkyl derivatives [1,2]. Reaction occurred at a convenient rate when pyridine—pyridine hydrochloride buffer was used. The solvolysis showed first order kinetics and produced stoichiometric amounts of haloform. The other products were: trimethylsilanol, trimethylpropoxysilane, and occasionally small amounts of hexamethyldisiloxane. The formation of all these products was monitored. Analysis of kinetic curves indicated that trimethylsilanol and trimethylpropoxysilane were formed directly in solvolysis; in other words hydrolysis and alcoholysis occurred concurrently, with hexamethyldisiloxane being formed by subsequent condensation of the silanol with the propoxysilane [4,5].

No reaction involving solvent conjugate base was detected under the conditions used (Fig. 1). Pyridine acts as a general base; the possibility of nucleophilic catalysis must be excluded in the light of the fact that 2,6-lutidine is 9 times as effective a catalyst than pyridine, since steric effects would give the opposite sequence of reactivity than for nucleophilic catalysis, involving direct attack of pyridine or its derivatives at silicon.

Spontaneous cleavage also occurred, and its rate was not affected the presence of strong acids such as HCl (Table 1). The overall process thus obeys the following rate law (where k_0 and k_c refer to the spontaneous and catalysed processes, respectively):

$$\frac{-\mathrm{d}[R_3SiCX_3]}{\mathrm{d}t} = \frac{\mathrm{d}[HCX_3]}{\mathrm{d}t} = (k_0 + k_c[\text{pyridine}])[R_3SiCX_3] \qquad (1)$$

X = Cl, Br

Solvent effect

The hydrolysis of (trihalomethyl)trimethylsilanes was also studied in dioxane—water system, where it again obeyed eq. 1. The rate of pyridine-catalysed reaction of Me_3SiCBr_3 was about five times faster in the dioxane—water (8 : 2 V/V)

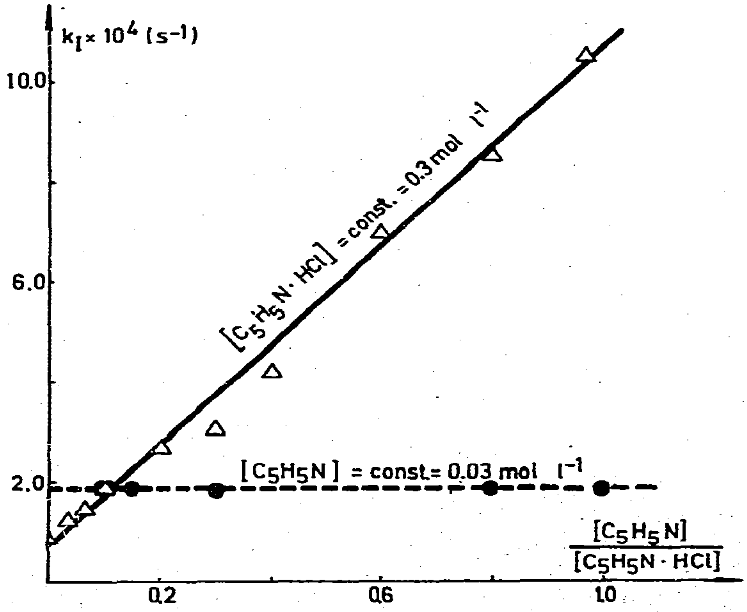


Fig. 1. Dependence of the observed first order rate constant on pyridine and pyridine hydrochloride concentration (Me_3SiCBr_3; 25°C).

TABLE 1

KINETIC RESULTS (n-PrOH/H_2O SYSTEM 8/2 V/V, $\mu = 0.4$, cm^{-1} temperature 25°C)

[pyridine] (*M*)	[pyridine · HCl] (*M*)	[HCl] (*M*)	$k_{obs} \times 10^6$ (s^{-1})	$k_0 \times 10^6$ (s^{-1})	$k_c \times 10^5$ ($l\ mol^{-1}\ s^{-1}$)
Silane: Me_3SiCCl_3 (0.13 M)					
—	0.30	—	2.33		
0.02	0.30	—	4.00		
0.06	0.30	—	8.00	2.45 ± 0.05	8.70 ± 0.05
0.12	0.30	—	13.20		
0.18	0.30	—	17.80		
Silane: Me_3SiCBr_3 (0.12 M)					
—	0.30	—	83		
0.01	0.30	—	127		
0.02	0.30	—	148		
0.03	0.30	—	188		
0.06	0.30	—	268		
0.09	0.30	—	300		
0.12	0.30	—	418		
0.18	0.30	—	697	80 ± 10	330 ± 10
0.24	0.30	—	850		
0.29	0.30	—	1050		
—	0.30	0.03	80		
—	0.30	0.10	82		
0.03	0.20	—	183		
0.03	0.10	—	178		
0.03	0.05	—	187		
0.03	0.03	—	183		
Silane:  *$Si(Me)CHBr_2$ [2,4-lutidine] [2,4-lutidine · HCl] (0.13 M)*					
0.15	0.33	—	88		
0.17	0.19	—	95		
0.30	0.67	—	175	—	57.3 ± 1.4
0.46	0.85	—	265		
0.53	1.42	—	295		

system, than in propanol—water (8 : 2 V/V), and the spontaneous hydrolysis was about 1.5 times faster (see Table 2). In terms of the dielectric constants, the reverse order of rates would be expected, since the reaction between the two uncharged molecules must involve some charge separation on going from the initial to the transition state, and this would be favoured in the more polar alcoholic system. (The spontaneous hydrolysis in polar aprotic DMSO is about two orders faster than in dioxane (Table 2), and part of this increase is probably due

TABLE 2

RATE CONSTANTS IN VARIOUS SOLVENTS (HYDROLYSIS) ([Me_3SiCBr_3] 0.12 *M*, [H_2O] 4.67 *M*, temperature 25°C)

Solvent	$k_0 \times 10^5$ (s^{-1})	$k_c \times 10^3$ ($l\ mol\ s^{-1}$)
n-PrOH	2.37	1.10
1,4-Dioxane	3.67	5.22
DMSO	362	—

to the increase in the dielectric constant.) It follows that specific solvation effects overwhelm general solvation effects related to the dielectric constant. To throw light on the nature of these interactions, the solvolyses in propanol and dioxane were examined at low water concentrations.

Use of GLC enables us to follow separately the formation of trimethylsilanol

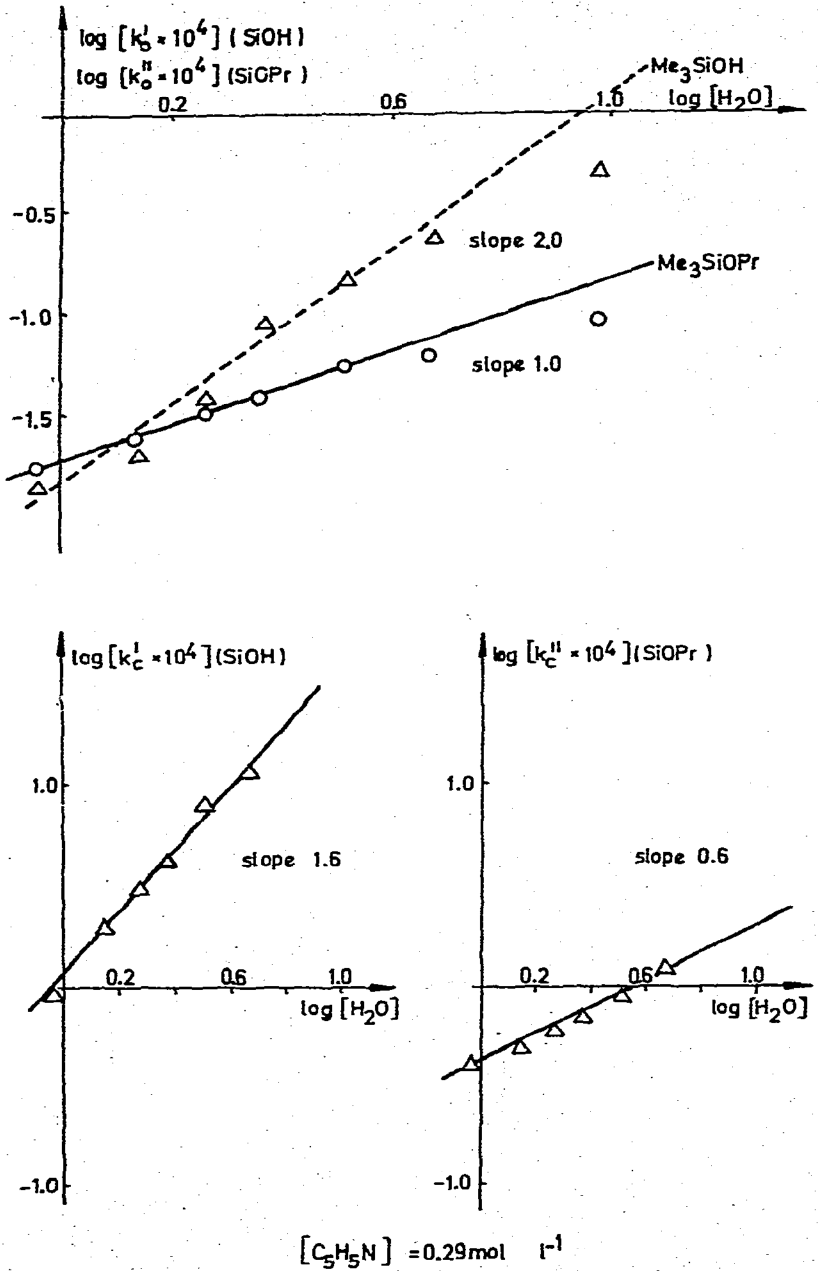


Fig. 2. Spontaneous and pyridine catalysed solvolysis of Me_3SiCBr_3 in aqueous propanol at 25°C. Plots of log K against log [H_2O] (k_0', k_c': spontaneous and catalysed hydrolysis; k_0'', k_c'': spontaneous and catalysed propanolysis).

(hydrolysis) and that of trimethylpropoxysilane (propanolysis). Runs for the tribromomethyl derivative at various water concentrations showed that for concentrations up to 5 mol l^{-1}, the order with respect to water was close to second for hydrolysis and close to first for propanolysis (Fig. 2).

No uncatalysed cleavage was observed in anhydrous propanol, and thus the presence of water is necessary for the spontaneous alcoholysis of (tribromomethyl)trimethylsilane. Propanolysis did occur smoothly, however, in the presence of pyridine under such conditions. In the range of water concentration studied equation 2 follows, where $(k_c'')_0$ = pyridine catalysed alcoholysis in anhydrous n-propanol (3.7×10^{-5} mol l s^{-1}) (25°C) and k_c'' = pyridine catalysed alcoholysis in propanol—water 8 : 2 V/V.

$$\frac{d[\equiv\text{SiOPr}]}{dt} = \{(k_c'')_0 + k_c'')[\text{H}_2\text{O}]^{0.6}\}[\text{pyridine}][\text{Me}_3\text{SiCX}_3] \qquad (2)$$

The pyridine-catalysed hydrolysis had an order of 1.6 with respect to water (Fig. 2). In dioxane as a solvent both the catalysed and the spontaneous reactions are of second order with respect to water (Fig. 3).

Silane structure

(Tribromomethyl)trimethylsilane reacted much faster than the chloro derivative in both the spontaneous and catalysed solvolyses, indicating that in both cases silicon—carbon bond cleavage occurs in the rate-determining step, and that the bond must be substantially broken in the transition state of this step. Increasing stabilisation of negative charge on the leaving group, associated with the higher polarizability of the bromine atom, is presumably mainly responsible for the larger reactivity of (tribromomethyl)trimethylsilane; a similar reactivity sequence was observed by Hine for base-catalysed isotope exchange in haloforms [6].

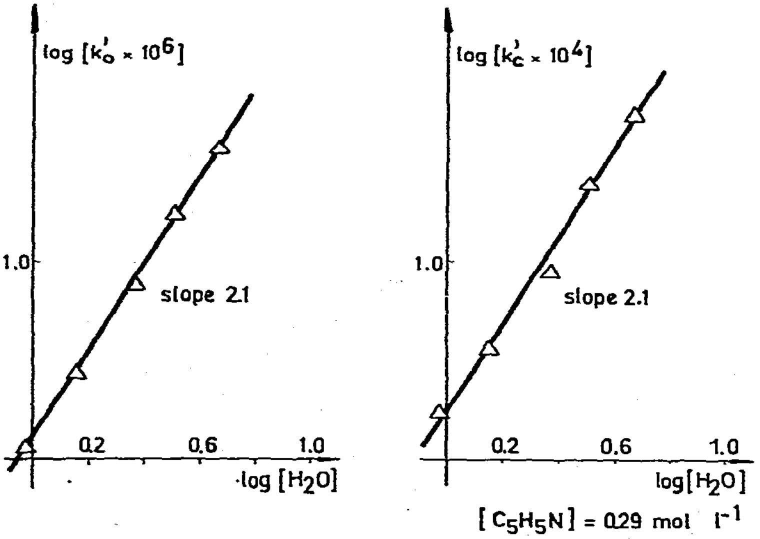


Fig. 3. Spontaneous and pyridine catalysed hydrolysis of Me_3SiCBr_3 in aqueous dioxane. Plots of log k against log H_2O (k_0', k_c': spontaneous and catalysed hydrolysis).

TABLE 3

SOLVOLYSIS OF Me_3SiCX_3 (X = Cl, Br) IN DIOXANE—WATER 8/2 V/V SYSTEM

	Me_3SiCCl_3		Me_3SiCBr_3	
	spontaneous process	catalysed process	spontaneous process	catalysed process
$\Delta H^{\ddagger}$(kcal mole^{-1})	7.0 ± 0.4	5.1 ± 0.4	5.6 ± 0.4	2.7 ± 0.2
$\Delta S^{\ddagger}$ (eu)	−60.1 ± 4.6	−62.2 ± 4.5	−63.5 ± 4.7	−66.0 ± 5.0
PIE	1.56	—	1.21	—
(k_H/k_D)solv.	2.02	1.39	3.14	1.72

Activation energies and entropies were determined for the hydrolysis in dioxane—water system. The entropy loss in transition state formation is large in both cases for the spontaneous and the catalysed processes. This is characteristic of the associative type of mechanism, involving a crowded transition state structure, formed from several species which were free in the initial state. The entropy loss is slightly larger for the bromo derivative, and the higher reactivity of (tribromomethyl)trimethylsilane is associated with a smaller enthalpy of activation. The small enthalpy of activation observed seems to be a common feature of the hydrolytic substitution at silicon in dioxane, and has been attributed partly to negative enthalpies of water complexation and partly to a higher degree of the saturation of bonding ability of silicon through its *d*-orbitals in the transition state [7]. It is noteworth that the nucleophilicity of water should be higher in dioxane than in a protic solvent as its oxygen lone pairs are not involved in hydrogen bonding.

α-Dihaloalkyl, which is a poorer leaving group cannot stabilize negative charge as effectively as α-trihalomethyl groups. Even in the presence of the much stronger base 2,4-lutidine, no cleavage of (dibromomethyl)trimethylsilane was observed in the propanol—water system. Reaction did occur, however, for 1-dibromomethyl-1-methylsilacyclobutane, and it was found to be subject to general base catalysis by lutidine. The silacyclobutyl ring was preserved. This unusual reactivity of silacyclobutanes towards nucleophilic substitution at silicon has been observed before and explained in terms of the special structure of these compounds which favours a frontal attack of the nucleophile at silicon [8].

Solvent isotope effects

The values of product isotope effect (PIE) for the spontaneous hydrolysis in dioxane, though not very large (see Table 3) point to electrophilic assistance in the cleavage of (trihalomethyl)trimethylsilanes. In the case of a poor leaving group such as CX_3 even small electrophilic assistance may lead to a considerable facilitation of Si—C cleavage, as suggested previously for benzyl derivatives [9—11]. In the spontaneous solvolysis in which the leaving group is displaced by a weak nucleophile the assistance seems to be especially important. Distinctly larger PIE values were observed for removal of the trichloromethyl group, which being a poorer leaving group than tribromomethyl requires more assistance from the solvent in the transition state. Detailed interpretation of kinetic solvent isotope effects (Table 3) would require separation of secondary and primary effects, which is difficult. As far as secondary effects are concerned, we must take into account that the nucleophilic attack is concerted with proton transfer from the nucleophile to a neutral molecule and leads in the transition state to the structure $=OL^{\delta+}$ for the spontaneous reaction or $\equiv NL^{\delta+}$ for the catalysed one (L = H or D). As $=OH^+$ is more effectively solvated than $=OD^+$, the k_H/k_D value connected with secondary solvent effect should be >1. This effect should be of minor importance for the catalysed process because the fractionation factors for =NL and $\equiv NL^+$ are comparable [12], and the lower values of the solvent isotope effect observed for pyridine catalysed cleavage is consistent with this. Taking into account these secondary effects and the PIE values, we may conclude that the primary effect associated with proton removal from attacking nucleophile is small, indicating an unsymmetrical position of the proton in the transition state. The larger kinetic solvent isotope effect is observed for (tribromomethyl)trimethylsilane in both the spontaneous and the catalysed reaction; according to the principle of microreversibility the poorer leaving group (trichloromethyl) requires a higher degree of proton transfer from the attacking nucleophile, and this leads to the conclusion that the extent of this proton transfer is large in the transition state [13]. To confirm it, we performed a series of runs with (tribromomethyl)trimethylsilane using various pyridine derivatives as catalysts. The data conform to the Brönsted catalysis law with a rather high value of β viz., 0.63. This value cannot be used as a quantitative measure of the extent of proton transfer as in the way the β values in water are used [14] but it provides confirmation for an advanced degree of proton transfer in the transition state, especially when a cyclic structure is assumed for the activated complex in which the proton acceptor in effect passes on the proton to the leaving group (see below).

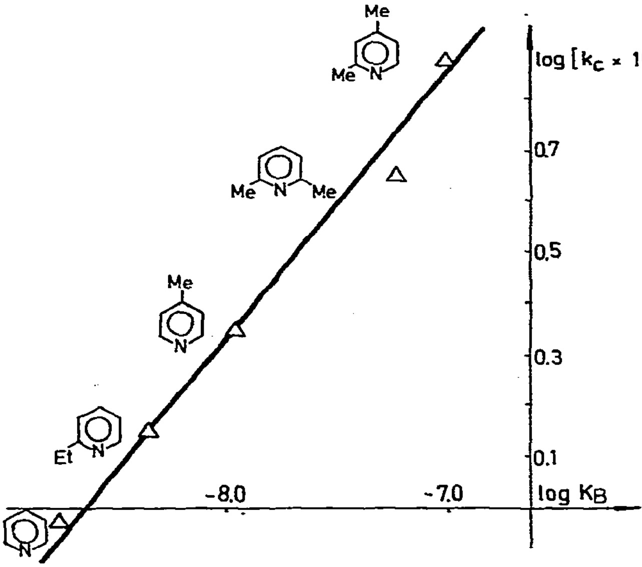
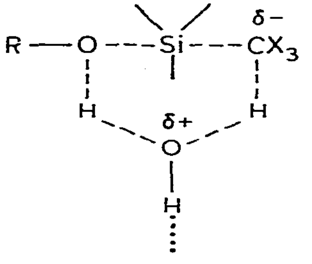


Fig. 4. Comparison of catalytic constants k_c with basicity constants K_B in Me_3SiCBr_3 hydrolysis (dioxane—water system 9 : 1 V/V, 25°C).

The nature of the transition states

The most striking feature of the results is the close similarity between the catalysed and spontaneous solvolyses. Both take a similar course in propanol— and dioxane—water solvents and the spontaneous and catalysed reactions in dioxane are both second order with respect to water. The interpretation of this order in water in terms of molecularity is dangerous because it ignores changes in medium effect which must be associated to the variable water content. It is somewhat justified here since the specific solvent interactions are more important than the bulk medium effects.

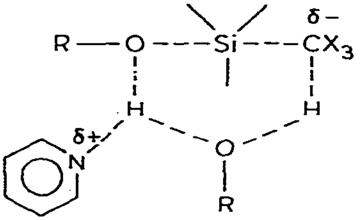
Because of lack of information about the state of water in its concentrated solutions, we cannot directly relate the order to the number of water molecules in the transition state but we can assume, that at least two such molecules are present in the transition state of the hydrolysis in propanol and dioxane. The kinetics points to three functions performed in the cleavage by the solvent species present: (i) a nucleophilic function performed by water or propanol. The ratio of the rate constants $(k(\mathrm{SiOH})/k(\mathrm{SiOPr}))_{\mathrm{cat.}} = 13.0$, and $(k(\mathrm{SiOH})/k(\mathrm{SiOPr}))_{\mathrm{spont.}} = 5.2$, at nearly equal water and propanol concentration (8 : 2 V/V Pr—OH : H_2O), shows that water is the more efficient nucleophile; (ii) electrophilic assistance to the leaving group; (iii) acceptance of the proton from the nucleophile, which in the catalysed process is performed by pyridine. The similarity between the spontaneous and catalysed solvolyses suggests a similarity between the structures of the transition states. We propose a multicentre cyclic structure for the transition states (I, II) * in which a hydrogen bonded complex functions as nucleophile and electrophile simultaneously.



(I)

spontaneous cleavage

R = n − Pr, H



(II)

catalysed cleavage

These structures explain an order of 2 in water observed for both the spontaneous and catalysed hydrolyses in dioxane. They are also in agreement with an order of 1 with respect to water in spontaneous propanolysis and the order of 2 with respect to water in the spontaneous hydrolysis in propanol.
In the transition state the species which perform a dual role of proton acceptor from the nucleophile and proton donor to the leaving group must carry a considerable positive charge, as there is evidence for a large degree of proton transfer from the nucleophile and a small degree of proton transfer from it to the leaving group. The positive charge is more effectively stabilized when carried by a water molecule, since propanol has no additional proton to hydrogen bond with the medium. Steric hindrance may also render electrophilic assistance by a propanol molecule less effective. Large steric effects associated with the electrophilic

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* Structures I and II are not intended to imply stereochemistry.

assistance to the leaving carbanion have been discussed earlier [11]. These two factors seem to act together to prevent the spontaneous cleavage of (trihalomethyl)trimethylsilanes in anhydrous propanol. In the catalysed process, an alcohol may compete with a water molecule as the proton donor to the leaving carbanion. This is because the positive charge in this case is located mainly on pyridine, and the stabilisation of the charge by the interaction with the medium is less important.

The following observations give further support to the proposal of the cyclic structure for the transition state:

1. The species rendering electrophilic assistance acts as a general acid, and the ability to yield a proton to the leaving group should be a function of its acidity. Thus the reaction should be subject to acid catalysis, but no such catalysis was detected even in the presence of 0.1 *M* HCl.
2. The formation of an open transition state structure would be accompanied by a considerable charge separation. The synchronous processes implied by cyclic structure would lead to a smaller charge generation and this is consistent with the observed medium effects.
3. The synchronous charge transfers in the cyclic system should lower the energy barrier and result in a decrease of structural freedom in the transition state; this is consistent with the low enthalpy and large negative entropy of activation.
4. The cyclic structure would favour the frontal attack of a nucleophile, and this would account for the abnormally high reactivity of the silacyclobutane derivative.

General base and base-nucleophile catalysis

Our studies of the solvolytic cleavage of Si—C bonds in α-haloalkylorganosilanes in the presence of ammonia and amines showed that the process is subject to general base catalysis, and includes a reaction with a solvent conjugate base [1,2], catalysis by a weak base, and finally a spontaneous reaction.

The base-nucleophile catalysis which was additionally observed in the presence of ammonia [1,2] seems to be one of the most interesting features. The mechanism involves ammonolysis of the Si—C bond followed by solvolysis of the unstable silylamine. In view of the similarity between the mechanisms of ammonolysis and simple solvolysis [2], it seems likely by analogy that ammonolysis could be catalysed not only by lyate ion but also by a weak base such as another molecule of ammonia. In order to check this possibility we examined the interaction of ammonia with (tribromomethyl)trimethylsilane in anhydrous dioxane. GLC analysis revealed the formation of hexamethyldisilazane and bromoform. In view of the ready condensation of trimethylsilylamine [15] the following reaction sequence, can be assumed:

$$Me_3SiCBr_3 + NH_3 \rightarrow Me_3SiNH_2 + CHBr_3$$

$$2\ Me_3SiNH_2 \rightarrow Me_3SiNHSiMe_3 + NH_3$$

By analogy with the mechanism of hydrolysis of α-trihaloalkyl derivatives, at least two NH_3 molecules must participate in this process, one acting as a nucleophile agent and the other acting as proton accepting species also providing electrophilic assitance to the leaving group. The spontaneous ammonolysis in dioxane may thus point to the generality of the mechanism proposed for base-nucleophile catalysis in a protolytic medium involving either lyate ion or weak base participation. However, the catalytic activity of weak bases is low and in aqueous ammonia the catalysis by lyate ion dominates.

In conclusion, the solvolytic cleavage of Si—C bonds in the presence of ammonia and amines can be described in terms of the general eq. 3, where B de-

$$\frac{-d[\text{Si—C}]}{dt} = \{k_0 + k_{\text{I}}[\text{B}] + k_{\text{II}}[\text{OR}^-] + k_{\text{III}}[\text{B}]^2 + k_{\text{IV}}[\text{B}][\text{OR}^-]\}\,[\text{substrate}] \qquad (3)$$

notes a weak base, and k_x denotes the catalytic constants for simple catalysis by weak base (x = I), simple catalysis involving solvent conjugate base (x = II), base-nucleophile catalysis by weak base (x = III), base-nucleophile catalysis involving solvent conjugate base (x = IV).

The relative contributions of the various types of catalysis are determined by the reaction medium, catalyst, and reagent structure. However, the differences in catalytic constants are large, and so it is difficult to observe more than two concurrent processes in any one solvolysis system.

Experimental

General

All solvents and reactants were carefully dried by standard procedures.

Preparation of Me_3SiCX_3 compounds

(Trichloromethyl)trimethylsilane was prepared from CCl_4 and Me_3SiCl in Mg/HMPT [16], and was recrystallized from anhydrous n-propanol.

(Tribromomethyl)trimethylsilane was made by free radical bromination of $Me_3SiCHBr_2$ with *N*-bromosuccinimide in the presence of benzoyl peroxide [17].

Preparation of 1-dibromomethyl-1-methylsilacyclobutane

This was prepared from 1-chloro-1-methylsilacyclobutane [18] by a low temperature Grignard reaction with dibromomethylmagnesium bromide using a standard procedure [19]. It was fractionated through a spinning band column and had a b.p. of 96°C/12 mmHg; NMR(CCl_4)τ (ppm) 4.61 s ($CHBr_2$); 7.84 m (CCH_2C); 8.74 m ($(CH_2)_2Si$); 9.47 s ($(CH_3)Si$). (Found: C, 23.50; H, 4.09; Br, 61.82. $C_5H_{10}Br_2Si$ calcd.: C, 23.27; H, 3.91; Br, 61.94%.) GLC revealed no significant quantities of impurities.

Rate measurements

The general procedure has been described [20]. The operating GLC conditions are shown in Table 4.

Measurement of product isotope effects.

A 10 mol. % solution of 1 : 1 H_2O—D_2O in dioxane was used as a solvent. A solution of Me_3SiCX_3 (0.5 *M*) was kept at constant temperature 25 ± 1°C. When the reaction was complete (as shown by GLC), samples were analysed by ^1H NMR spectroscopy using a NMR Perkin—Elmer R-128 spectrometer. The PIE values were given by $[CHX_3]/[Me_3SiCX_3] - [CHX_3]$.

TABLE 4

GLC ANALYSIS

Silane	Compound determined	Internal standard	Column	Temperature		
				Inj.	Col.	Det.
Si(Me)CHBr$_2$	CH$_2$Br$_2$	cumene	15% LAC-296/Chromosorb PAW	150	105	175
Me$_3$SiCCl$_3$	CHCl$_3$	n-BuCl	15% LAC-296/Chromosorb PAW	190	75	240
Me$_3$SiCBr$_3$	CHBr$_3$	CH$_2$I$_2$	20% OV-101/Chromosorb WAW	190	120	240
Me$_3$SiCCl$_3$ Me$_3$SiCBr$_3$	Me$_3$SiOSiMe$_3$ Me$_3$SiOPr Me$_3$SiOH	n-BuCl	15% LAC-296/Chromosorb PAW	190	75	240

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