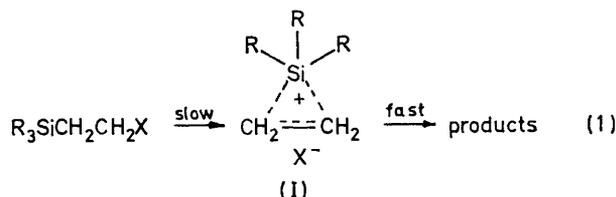


## The Solvolytic Fragmentation of Trialkoxy-2-halogenoethylsilanes

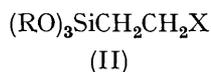
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Trialkoxy-2-halogenoethylsilanes decompose in alkaline solution to give ethylene by a hydroxide ion-catalysed reaction, whereas in acid solutions these compounds undergo rapid hydrolysis to 2-halogenoethylsilanetriols which then undergo fragmentation by both uncatalysed and hydroxide ion-catalysed reactions.

THE fragmentation of 2-halogenoethyltrimethylsilanes has been suggested by Baughman<sup>1</sup> to proceed *via* ionization of the C-X bond. Later, the work of Jarvie<sup>2</sup> and Eaborn<sup>3</sup> and their co-workers indicated that the rapid solvolysis of such compounds is due to anchimeric assistance by the silicon atom, and that a silicon-bridged intermediate (I) was involved [equation (I)].



It was thought that similar compounds bearing electro-negative silicon substituents would be unlikely to follow this reaction pathway, but might undergo a base-catalysed fragmentation. Accordingly the reactions of some trialkoxy-2-halogenoethylsilanes (II) in alkaline solution have been investigated.



### EXPERIMENTAL

**Materials.**—2-Chloroethyltrimethoxysilane, b.p. 112° at 100 mmHg, and 2-chloroethyltriethoxysilane, b.p. 101–102° at 20 mmHg, were prepared by the method of Boye and Post.<sup>4</sup>

**2-Bromoethyltrichlorosilane.**—Hydrogen bromide was passed into a solution of benzoyl peroxide (1 g) in trichloro-(vinyl)silane (100 g) at 0–5°. After 25 g had been absorbed further benzoyl peroxide (1 g) was added and the reaction was continued until a total of 60 g of HBr had been absorbed. The product was then distilled to give 2-bromoethyltrichlorosilane (122 g, 81%), b.p. 169–172° (lit.,<sup>5</sup> 171°).

**2-Bromoethyltrimethoxysilane.**—Methanol (22 g) was added dropwise to 2-bromoethyltrichlorosilane (50 g) at room temperature. When addition was complete the mixture was heated at 100° until no further HCl was evolved (3 h). The product was distilled to give 2-bromoethyltrimethoxysilane (41 g, 77%), b.p. 125–126° at 100 mmHg (Found: C, 26.3; H, 5.7; Br, 34.5. C<sub>5</sub>H<sub>13</sub>BrO<sub>3</sub>Si requires C, 26.2; H, 5.7; Br, 34.9%).

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<sup>1</sup> G. A. Baughman, *Diss. Abs.*, 1961, **22**, 2187.

<sup>2</sup> A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. (B)*, 1969, 852.

<sup>3</sup> M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 301.

**Ethylene.**—Yields of ethylene were determined by solvolysing 2-chloroethyltrimethoxysilane in 0.1M-phosphate or -borate buffers at 25° in vessels of known volume. After reaction was complete, the ethylene content of the air space was estimated using g.l.c. (150 × 0.4 cm Durapak OPN column operating at 50°). The yields at three pH values are given in Table 1.

**Kinetics.**—(a) *Solvolysis measurements.* These were carried out using a Radiometer pH stat. Reactions were initiated by injecting 0.1 ml of a stock solution of the silane in the corresponding alcohol into 3 ml of 0.1M-KCl solution at the required pH. The concentration of the silane in the reaction solution was ca. 2 × 10<sup>-3</sup>M. As the solvolysis proceeded the pH was maintained by the addition of 0.01M-KOH. Below pH 8 the silane produced one equiv. of acid, but the yield increased above this pH due to ionization of the silicic acid produced.

Rate determinations using methanol-water mixtures were made by titration using Bromothymol Blue as indicator (Table 2).

Solutions of 2-halogenoethylsilanetriols were prepared by allowing aqueous solutions of the corresponding trialkoxy- or trichloro-silanes to stand at pH 3 for 15 min at room temperature. Kinetic measurements had indicated the hydrolysis to be essentially complete after this treatment. The pH was then raised to the required value for solvolysis studies.

Rate constants (*k*<sub>obs</sub>) were calculated from the integrated first-order rate equation in the usual manner, but for very slow reactions the Guggenheim method was used.

The values of the ionic product for water, used to convert *k*<sub>obs</sub> to the corresponding bimolecular rate constants were those of Harned and Fallon.<sup>6</sup>

Activation parameters were measured from rate constants at four temperatures in the range 20–50°.

(b) *Acid-catalysed hydrolysis of 2-chloroethyltrimethoxysilane.* Solutions of the alkoxy-silane were allowed to react at the required pH for various times. The pH was then raised to 8.0 and the solvolysis of the mixture was carried out as above. The titre rose rapidly at first, then increased slowly.

By treating the results in the manner described by Frost and Pearson<sup>7</sup> for a mixture of parallel reactions, it was possible to estimate the original composition of the mixtures, and hence obtain the rate constants for acid-catalysed hydrolysis of the silane. A typical first-order plot obtained in this manner is shown in Figure 1.

<sup>4</sup> F. C. Boye and H. W. Post, *J. Org. Chem.*, 1951, **16**, 391.

<sup>5</sup> V. F. Mironov, V. V. Nepomnina, and L. A. Leites, *Izvest. Acad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1960, 461 (*Chem. Abs.*, 1960, **54**, 22,328).

<sup>6</sup> H. S. Harned and L. D. Fallon, *J. Amer. Chem. Soc.*, 1939, **61**, 2374.

<sup>7</sup> A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, London, 1961, 2nd. edn., p. 162.

## RESULTS AND DISCUSSION

The solvolysis\* of 2-chloroethyltrimethoxysilane (II; R = Me, X = Cl) in basic solutions was found to give

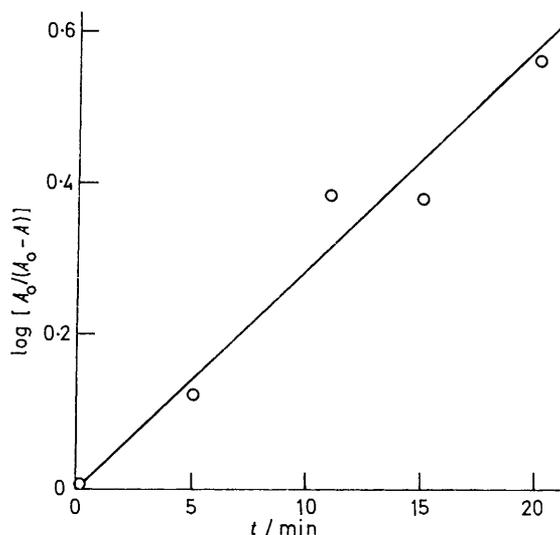
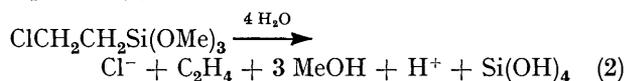


FIGURE 1 First-order plot for the acid-catalysed hydrolysis of 2-chloroethyltrimethoxysilane at pH 5.15 at 25°.  $A$  = concentration of silane,  $A_0$  = initial silane concentration =  $3.56 \times 10^{-3}$

essentially quantitative yields of ethylene and acid (Table 1). The overall reaction can be described by equation (2).



The rate constant for disappearance of the trialkoxysilane at a given pH,  $k_{\text{obs}}$ , measured by following the

TABLE 1

Yields of ethylene from solvolysis of 2-chloroethyltrimethoxysilane at 25°

pH	6.65	7.7	9.2
Yield (%)	101	99	93

liberation of acid, is not a simple function of the hydroxide ion concentration, as is shown by the variation of

TABLE 2

Pseudo-first-order rate constants for the spontaneous solvolysis of 2-chloroethyltrimethoxysilane in methanol-water at 50°

MeOH (%v/v)	0	20	40	50	60
$10^5 k_0 / \text{s}^{-1}$	44	24	11	8.8	5.2

$\log k_{\text{obs}}$  with pH (Figure 2). The solvolysis of 2-bromoethyltrimethoxysilane (II; X = Br, R = Me) followed a very similar pattern.

At pH > 7, the reactions appeared to be simple hydroxide ion-catalysed reactions. The second-order rate constant,  $k_{\text{OH}'}$ , for 2-chloroethyltriethoxysilane (II; R =

\* The term 'solvolysis' is used here to describe any reaction which, overall, liberates acid, while the terms 'fragmentation' and 'hydrolysis' refer respectively to olefin-forming reactions and nucleophilic displacements at silicon by lyate species.

Et, X = Cl) was found to be slower than that for the corresponding trimethoxysilane by a factor of 38 (Table 3). This is consistent with the reaction involving attack

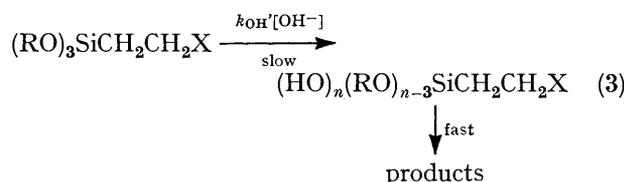
TABLE 3

Rate constants and activation parameters for the decomposition of  $\text{XCH}_2\text{CH}_2\text{Si}(\text{OR})_3$  at 25° in water with  $\mu = 0.1\text{M}$

X	R	$10^{-2} k_{\text{H}} / \text{l mol}^{-1} \text{s}^{-1}$	$10^{-3} k'_{\text{OH}} / \text{l mol}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger_{\text{OH}} / \text{kJ mol}^{-1}$	$\Delta S^\ddagger_{\text{OH}} / \text{J mol}^{-1} \text{K}^{-1}$
Cl	Me	2	1.28	$0 \mp 8$	$-192 \mp 30$
Cl	Et		0.0365		
Br	Me	1.2	1.35	$0 \pm 8$	$-192 \pm 30$

by hydroxide ion at silicon at such reactions would be expected to show marked steric effects.<sup>8a</sup>

However, 2-bromoethyltrimethoxysilane reacted only marginally (5%) faster than the corresponding chloro-compound. This lack of a large increase in rate suggests that the rate-limiting step in this reaction does not involve C-X fission, and possibly represents hydrolysis of the trialkoxysilane, followed by a rapid fragmentation of the product [equation (3)]. Alternatively, the lack



of sensitivity of the rate to the leaving group could indicate that addition of hydroxide ion to silicon, giving a

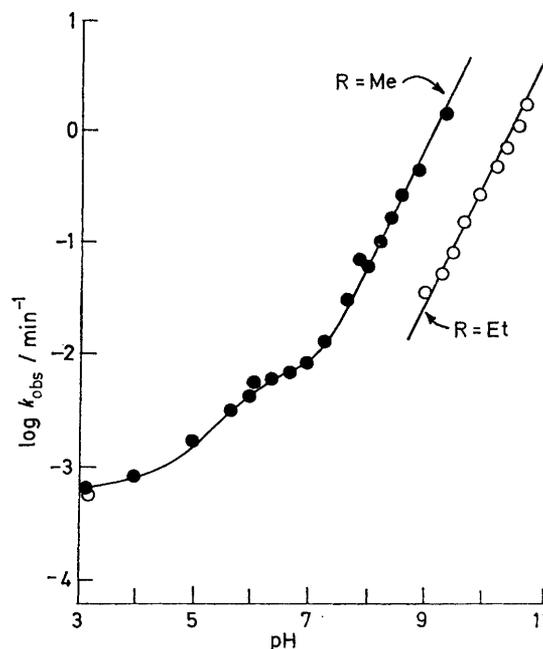
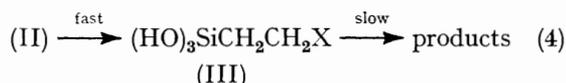


FIGURE 2 The variation in the rate of solvolysis of  $(\text{RO})_3\text{SiCH}_2\text{CH}_2\text{Cl}$  with pH, in water at 25° ( $\mu = 0.1\text{M}$ )

pentavalent adduct, could be rate limiting. The hydroxide ion-catalysed reaction will, for convenience, be described as a hydrolysis reaction for the present.

<sup>8</sup> See C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960 (a), p. 110; (b) p. 301.

In acid solution these changes in reactivity were reversed. Thus at pH 3 the rates of solvolysis of 2-chloroethyl-trimethoxy- and -triethoxy-silanes were the same, whereas 2-bromoethyltrimethoxysilane reacted some 13 times faster than the corresponding chloroethylsilane. Furthermore, the fourth mole of acid from solvolysis of 2-chloroethyltrichlorosilane was formed at the same rate as the acid liberated from the alkoxy-silanes. These findings indicate that the reaction being followed in acid solution was not solvolysis of the alkoxy-silanes, but of a common derivative. In dilute aqueous solution this derivative is most likely to be the 2-halogenoethylsilanetriol (III), and the reaction sequence involved is that in equation (4).



The evidence described so far is consistent with the fragmentation of trialkoxy-2-halogenoethylsilanes involving a two-stage process in which either hydrolysis of the trialkoxysilane or fragmentation of a hydrolysis product is rate limiting, depending on the pH. In order to confirm this it was necessary to show that in alkaline solution the silanetriols (III) underwent rapid fragmentation, and to identify the reason for the change in the rate-limiting step.

The change in the rate-limiting step is presumably due to the incursion of acid-catalysed hydrolysis of the trialkoxysilane, which would be expected from the results of other workers.<sup>8b</sup> A direct method of determining the rates of the acid-catalysed hydrolysis could not be found, but the solvolysis of partially hydrolysed 2-chloroethyltrimethoxysilanes could be used to obtain a rough estimate of these rates, and hence the rate constant for the acid-catalysed hydrolysis,  $k_H$ . The V shaped pH profile calculated from equation (5), using the appropriate

$$k_{\text{hydrolysis}} = k_H[H^+] + k_{OH^-}[OH^-] \quad (5)$$

rate constants  $k_H$  and  $k_{OH^-}$  (Table 3), for the hydrolysis of 2-chloroethyltrimethoxysilane is shown in Figure 3.

If the reaction of trialkoxy-2-halogenoethylsilanes in acid solution leads initially to hydrolysis, not fragmentation, it should be possible to prepare solutions of the hydrolysis products, which are presumed to be silanetriols, and to study the solvolysis behaviour of these.

The hydrolysis of trialkoxy-2-halogenoethylsilanes in acid solution led to the formation of a reactive product, which could not be satisfactorily identified. Removal of the water from hydrolysed solutions left a gummy material, which on extensive drying formed an insoluble powder. The rates of acid production from hydrolysed 2-chloroethyl-trimethoxy-, -triethoxy-, and -trichlorosilanes were, within experimental error, identical at all pH values, suggesting that all three silanes gave the same hydrolysis product, which is probably the silanetriol or a polymer thereof. In such dilute solutions polymerization is not likely, and the hydrolysis product is thought to be the silanetriol (III).

It was found that the solvolysis of these products obeyed the rate equation (6) where S represents the

$$-d[S]dt = (k_0 + k_{OH^-}[OH^-])[S] \quad (6)$$

silanetriol. It will be seen from Figure 3 that a combination of the hydrolysis rate of the trialkoxysilane [equation (5)] and the fragmentation rate of the silanetriol

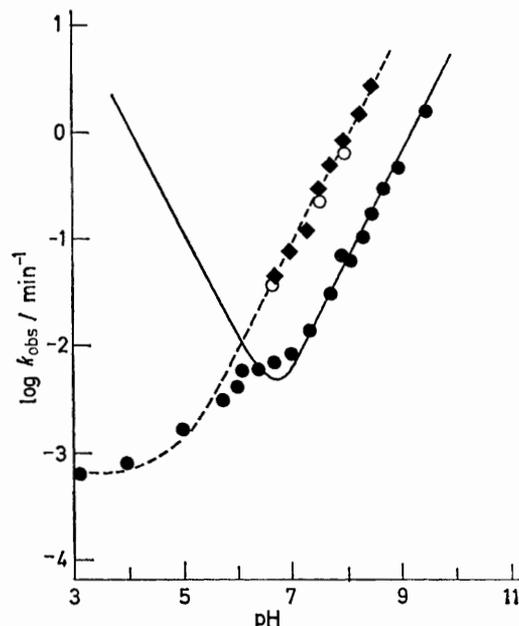


FIGURE 3 The variations in pseudo-first-order rate constants with pH for (a) overall solvolysis of  $(MeO)_3SiCH_2CH_2Cl$  (●); (b) 'hydrolysis' of  $(MeO)_3SiCH_2CH_2Cl$ , according to equation (5) (solid line); and (c) fragmentation of  $(HO)_3SiCH_2CH_2Cl$ , according to equation (6) (broken line). The symbols on (c) refer to reactions of the triol generated from the trimethoxy- (◆) and trichloro (○) silanes. All reactions were carried out at 25° with  $\mu = 0.1M$ .

[equation (6)] adequately explains all the features of the solvolysis of 2-chloroethyltrimethoxysilane in aqueous solution. The behaviour of 2-bromoethyltrimethoxysilane can be explained in a similar manner.

The fragmentation of the silanetriols (III; X = Cl or Br) proceeded by a spontaneous and a hydroxide ion-catalysed reaction, according to equation (6). In both reactions, 2-bromoethyltrimethoxysilane reacted 12–13

TABLE 4  
Rates of fragmentation of  $XCH_2CH_2Si(OH)_3$  at 25°  
( $\mu = 0.1M$ )

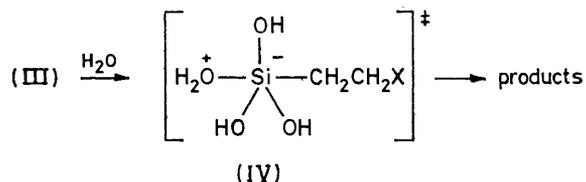
X	$10^7 k_0 / l \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-4} k_{OH^-} / l \text{ mol}^{-1} \text{ s}^{-1}$
Cl	1.84 <sup>a,d</sup> 2.10 <sup>b</sup> 1.93 <sup>c</sup>	1.38 <sup>b,e</sup>
Br	23.3 <sup>a</sup>	16.6

Silanetriols were generated from  $XCH_2CH_2SiY_3$  where <sup>a</sup> Y = OMe, <sup>b</sup> Y = OEt, and <sup>c</sup> Y = Cl. <sup>d</sup>  $\Delta H^\ddagger = 102 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -42 \text{ J mol}^{-1} \text{ K}^{-1}$ . <sup>e</sup>  $\Delta H^\ddagger = 61 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +25 \text{ J mol}^{-1} \text{ K}^{-1}$ .

times (Table 4) as fast as the 2-chloroethylsilane indicating that C–X bond fission occurs in the transition states.

For the spontaneous reaction, both the entropy of activation (Table 4) and the Grunwald–Winstein  $m$  value,

(0.5) were typical of a bimolecular reaction between water and the silanetriol. It is apparent that the replacement of methyl by hydroxy-groups on silicon results in a change of mechanism from ionization of the C-X bond to a concerted bimolecular reaction. The low  $m$  value found suggests that only a moderate amount of charge dispersal has taken place in the transition state, which probably resembles a pentavalent silicon species [*e.g.*



(IV)]. Whether or not an *intermediate* of structure (IV) precedes this transition state cannot be decided on the available evidence.

The entropy of activation for the hydroxide ion-catalysed reaction is in accord with a transition state corresponding to the conjugate base of (IV), derived by co-ordination of hydroxide ion onto silicon. It seems likely therefore that both these reactions are examples of a nucleophilic displacement at silicon where the 2-halogenoethyl group acts as a complex leaving group.

A bimolecular fragmentation reaction similar to those described above was originally postulated by Sommer and his co-workers<sup>9</sup> but this view appears to have been neglected. It would appear that  $\beta$ -eliminations involving silicon, like those involving hydrogen, proceed by more than one pathway.

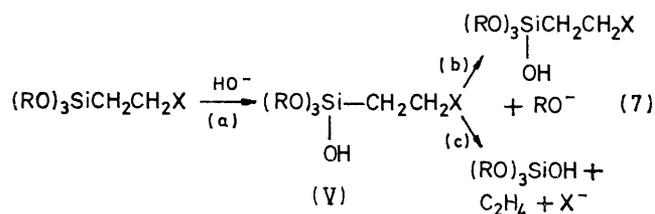
*Hydrolysis or Fragmentation of Trialkoxysilanes in Alkaline Solutions?*—The reaction of trialkoxysilanes (II) in alkaline solutions, which leads, overall, to frag-

<sup>9</sup> L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1083.

mentation, was described in the preceding section as a hydrolysis reaction. It must be emphasized that there is no rigorous proof that this is the case. The steric retardation and the lack of sensitivity of the rate of reaction to the leaving group are consistent with both a two step mechanism such as (3) and with rate-limiting co-ordination of hydroxide ion onto silicon to form the adduct (V). This adduct can undergo either fragmentation or loss of alkoxide, the latter leading to hydrolysis [equation (7)].

The fragmentation of the silanetriols can also be described by equation (7), but in this case the rate-limiting step must be the decomposition of (V; R = H) *via* pathway (c).

However, if step (a) is rate limiting for the trialkoxysilanes the initial reaction products will be determined only by the relative rates of steps (b) and (c), and there seems, at present, no way of differentiating between these.



In summary, the solvolysis of trialkoxy-2-halogenoethylsilanes in aqueous solution can occur by a number of mechanisms, in which both hydrolysis and fragmentation play significant roles in determining the kinetic behaviour. The relative importance of the two types of reaction will presumably depend on the nature of the silicon substituents and the leaving group on carbon.

I thank the Board of NRPRA for permission to publish these results.

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