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RATES AND MECHANISM OF SOLVOLYSIS OF *N*-PHENYLCYCLOSILAZOXANES *

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Summary

The rates of solvolysis of some *N*-phenyl-1-aza-3,5-dioxa-2,4,6-tris(dimethylsilyl)cyclohexanes, substituted in the benzene ring, have been measured spectrophotometrically in methanol containing a small quantity of water. The reaction is subject to general acid catalysis and is inhibited by weak bases. Electron-donating substituents accelerate the solvolysis. The ρ-constant, derived from the linear relation between the logarithms of the rate constants and Hammett σ constants is -1.2 ($\rho = -1.0$ in a neutral medium). A reverse deuterium isotope effect has been found ($k_H/k_D = 0.82$). The proposed mechanism for the Si–N bond cleavage, and the associated ring-opening, involves simultaneous nucleophilic attack of a solvent molecule on silicon and electrophilic assistance by proton transfer from the catalysing acid to the nitrogen.

Introduction

Studies on the mechanisms of heterolysis of the silicon–nitrogen bond have been the subject of a number of papers, which have been mainly concerned with silylamines, and have included the effects of substituents at silicon and nitrogen on the rate and also the effects of acid-base catalysis and the reaction medium [1–8]. In spite of the high reactivity of silylamides in silylation, most of the studies of this class of Si–N compounds, starting from the earliest [9,10], have dealt rather with structural aspects, and only a few have included rate measurements [11,12]. The kinetic studies of the reactivity of rings with a Si–N linkage have been concerned only with cyclosilazanes, $(R_2SiNH)_n$, containing secondary nitrogens, and have been limited to nucleophilic exchange at silicon in alcoholysis and acidolysis in neutral and weakly solvating solvents [13–15]. The mechanistic implications have been based on the polar effects of substituents in the attacking nucleophile. A four-centre

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* This paper is affectionately dedicated to Professor Raymond Calas on the occasion of his 70th birthday in recognition of his outstanding researches in organometallic chemistry during more than 30 years.

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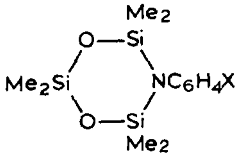
mechanism has been suggested, involving simultaneous attack on nitrogen and nucleophilic attack on silicon by the reagent.

We have thought it interesting to investigate kinetically the cleavage by methanol of the silicon–nitrogen bond in the compound *N*-phenyl-5-aza-1,3-dioxa-2,4,6-tris(dimethylsilyl)cyclohexane and its derivatives with substituents in the benzene ring, I, which are referred to in this paper as cyclosilazoxanes.



X = H, *m*- and *p*-CH_3, OCH_3, Cl, Br

(I)

We have previously reported the preparation of the parent compound, (I, X = H) [16] and its use as a monomer for synthesizing new organosilicon polymers of high thermal stability [17].

Results and discussion

The rates were measured in solvolytic conditions in methanol with an acetate buffer as catalyst. In order to avoid the effect of adventitious moisture, a fixed amount of water (1% v/v 0.56 *M*) was added in most runs. The proportion of added water was limited in order to maintain good solubility of the cyclosilazoxanes and to keep the rates within measurable limits, since water has an accelerating effect. The ionic strength of the solution was kept constant ($I = 0.02$) by adding calculated amounts of lithium chloride. The progress of the reaction was followed by making use of the differences in the UV spectra of *N*-aryl-cyclosilazoxanes and substituted anilines, the aromatic products of the reaction (Fig. 1).

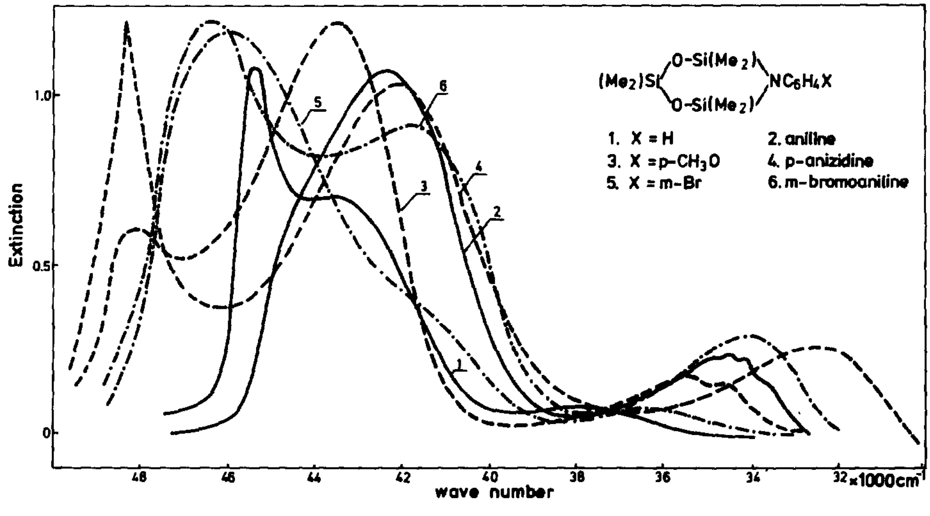
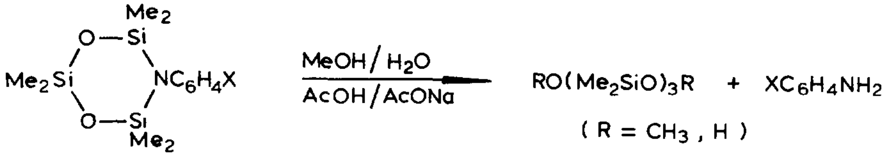


Fig. 1. UV spectra of the *N*-arylcyclosilazoxanes (I) and respective anilines, $XC_6H_4NH_2$.

It has been shown by gas-liquid chromatography and mass spectrometry that in the slightly acidic aqueous-methanolic medium the silicon–nitrogen bonds are cleaved and the siloxane system is preserved according to the following scheme:



In order to get some insight into the mechanism, the following kinetic tests were applied: the effect of acid-base catalysis, LFER analysis of the rates, and determination of activation parameters and the kinetic solvent isotope effect. At fixed concentrations of buffer and lithium chloride, or with no catalyst added, the reaction was found to be pseudo-first-order in cyclosilazoxane up to high conversion (over 90%). Overall first-order kinetics were also established (Figs. 2 and 3).

At constant ionic strength the experimental pseudo-first-order rate constant k_I is proportional to: 1) the concentration of acetic acid at constant buffer ratio (or, equivalently, at constant sodium acetate concentration), and 2) the buffer ratio at constant acid concentration (Figs. 4a and b). Thus the system is subject to general acid catalysis and the above relationships can be summarized by the following general form of the rate law:

$$-\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}t} = \left(k_0 + k_{\mathrm{AcOH}}[\mathrm{AcOH}] + k_{\mathrm{R\overset{+}{O}H_2}}[\mathrm{R\overset{+}{O}H_2}] + \Sigma k_\mathrm{B}[\mathrm{B}]\right)[\mathrm{S}]$$

$$[\mathrm{R\overset{+}{O}H_2}] = K_{\mathrm{AcOH}}\frac{[\mathrm{AcOH}]}{[\mathrm{AcONa}]}\,;\ k_\mathrm{B} \simeq 0$$

$$-\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}t} = \left(k_0 + k_{\mathrm{AcOH}}[\mathrm{AcOH}] + k'_{\mathrm{R\overset{+}{O}H_2}}\frac{[\mathrm{AcOH}]}{[\mathrm{AcONa}]}\right)[\mathrm{S}]$$

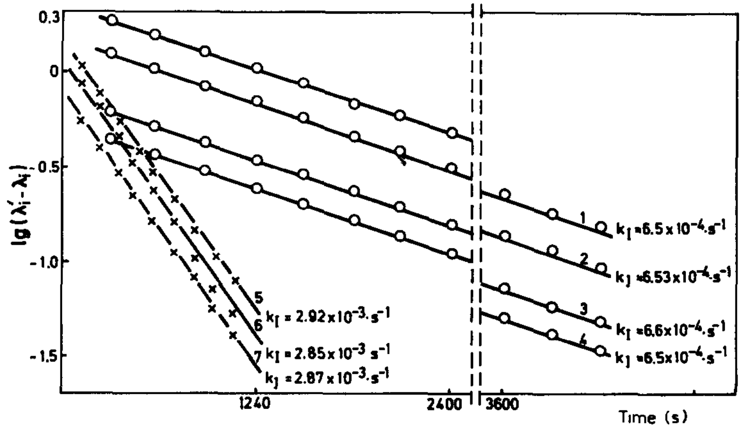


Fig. 2. Reaction order determination of solvolysis of *N*-arylcyclosilazoxanes [I]. Lines 1–4: MeOH; [AcOH] 0.025 *M*; [AcONa] 0.0025 *M*; $I = 0.02$; T 30°C; initial concentrations of silazoxanes, (10^4 *M*): 1, 9; 2, 6; 3, 3; 4, 2. Lines 5–7: MeOH/H_2O; [H_2O] 0.56 *M*; [AcOH] 0.05 *M*; [AcONa] 0.005 *M*; $I = 0.02$; T 30°C; Initial concentrations of silazoxanes, (10^4M): 5, 6; 6, 5; 7, 2.7.

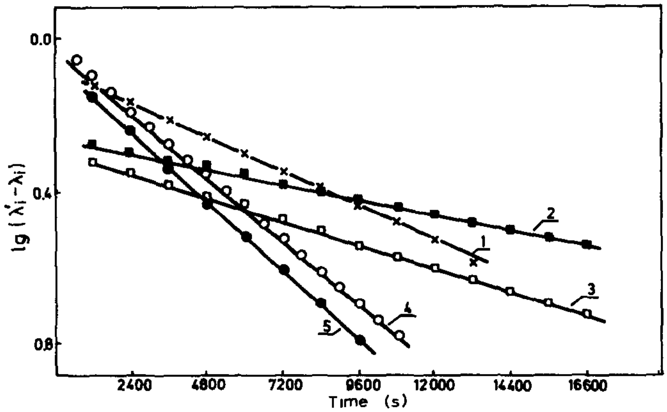


Fig. 3. Reaction orders for uncatalyzed solvolysis of *N*-arylcyclosilazoxanes $(Me_2Si)_3O_2NC_6H_4X$ in aqueous methanol, $[H_2O]$ 0.56 *M*; $I = 0.02$; *T* 25°C. Lines 1, X = H, C_0 3.8×10^{-4} *M*; 2, X = *m*-Br, C_0 2.7×10^{-4} *M*; 3, X = *p*-Br, C_0 3.4×10^{-4} *M*; 4, X = *p*-CH_3O, C_0 4.2×10^{-4} *M*; 5, X = *p*-CH_3, C_0 5×10^{-4} *M*; C_0 = initial concentration of silazoxane.

where $k'_{R\overset{+}{O}H_2} = k_{R\overset{+}{O}H_2} K_{AcOH}$

S represents the substrate; B, the base; k_0, the rate constant for catalysis by solvent molecules ("spontaneous reaction"); k_{AcOH}, the partial catalytic constant for catalysis by undissociated acid; $k_{R\overset{+}{O}H_2}$, the partial catalytic constant for catalysis by oxonium ions; and $k'_{R\overset{+}{O}H_2}$, the apparent partial catalytic constant for catalysis by oxonium ions. For I, X = H; $I = 0.02$ and $[H_2O] = 0.56$ *M* at 298 K; $k_0 = 1.07 \times 10^{-4}$ s^{-1}; $k_{AcOH} = 1.07 \times 10^{-2}$ M^{-1} s^{-1}; $k_{R\overset{+}{O}H_2} = 1.92 \times 10^{-4}$ s^{-1} ($k_0 = 1.02 \times 10^{-4}$ s^{-1} in a run with no catalyst added). The values of k_{AcOH} and $k_{R\overset{+}{O}H_2}$ were calculated from the slopes of the plots in Fig. 4. The approximate value of the dissociation constant of acetic acid in methanol-water can be evaluated from the relationship given by Shedlovsky and Kay [18]. For $[H_2O] = 0.56$ *M*, $K_{AcOH} \cong 10^{-9}$ *M*, which gives $k_{R\overset{+}{O}H_2} \cong 10^5$ M^{-1} s^{-1}. The value of k_0 was obtained either by extrapolation to zero buffer ratio of the function $z = k_0 + k'_{R\overset{+}{O}H_2}$ [AcOH]/[AcONa] (Fig. 4a) or by

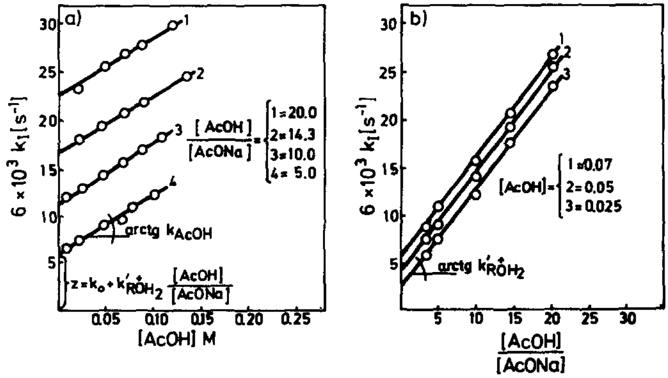


Fig. 4. Effect of the concentration of the catalysing system on the observed pseudo-first-order rate constant of solvolysis of *N*-phenyl-5-aza-1,3-dioxane-2,4,6-tris(dimethylsilyl)cyclohexane in aqueous methanol, $[H_2O]$ 0.56 *M*; $I = 0.02$; *T* 25°C.

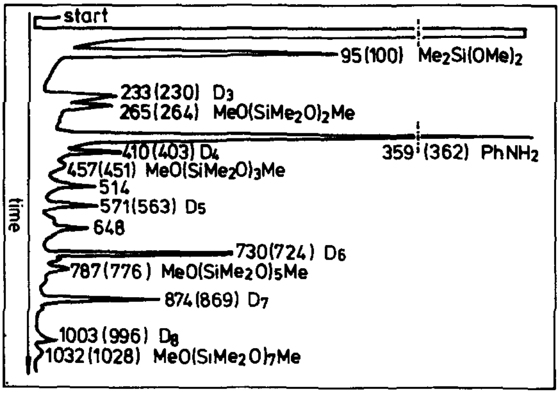


Fig. 5. Gas liquid chromatogram of the reaction mixture from the basic solvolysis of *N*-phenylcyclosilazaoxane (I, X = H) in aqueous methanol after 40 min reaction time, $[H_2O]$ 0.56 *M*, [NaOH] 0.5 *M*. Figures on the peaks: retention times of constituents of the mixture and (in parenthesis) of the original samples. D = $(CH_3)_2O$.

determining the experimental rate constant in a run with no catalyst added.

In a weakly basic medium of ammonia buffer or acetate buffer containing 80% sodium acetate, the reaction is strongly inhibited. Within a wide range of concentrations of ammonia buffer (10^{-4} to 4 *M*), or acetate buffer (6×10^{-3} to 0.5 *M*), no changes in the UV absorption were observed over long periods. It was impossible to investigate the effect of the strong base, NaOH, since its addition resulted in simultaneous cleavage of silazane and siloxane bonds, with subsequent condensations, as it is seen from the chromatogram (Fig. 5). The reaction mixture contains the series of dimethoxysiloxanes $MeO(SiMe_2O)_nMe$ ($n = 1$ to 7), and the products of cyclic condensations $(Me_2SiO)_m$ ($m = 3$ to 8). Small amounts of sodium acetate alone produced a systematic deceleration of the reaction: for example, the observed rate constant, k_I, for I, X = H ($I = 0.02$ and $[H_2O] = 0.56$ *M* at 298 K) at 0.0001, 0.001 and 0.04 *M* AcONa are (10^5 k_I, s^{-1}): 4.75, 2.10 and 0.867, respectively.

Small amounts of water, up to 0.1 *M*, do not affect the rate. However, with

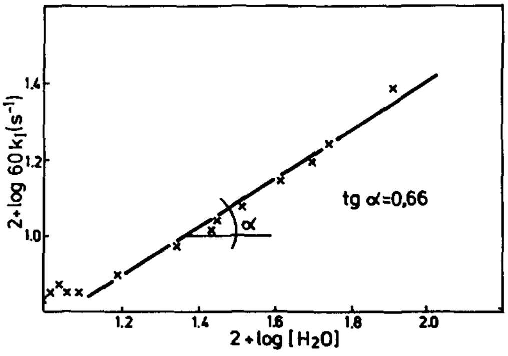


Fig. 6. Effect of water on the rate constant of solvolysis of *N*-phenyl-5-aza-1,3-dioxa-2,4,6-tris(dimethylsilyl)cyclohexane in methanol, [AcOH] 0.05 *M*; [AcONa] 0.005 *M*; $I = 0.02$; *T* 25°C.

further increase of water concentration the reaction is accelerated and the order in water, calculated from the slope in Fig. 6, is 0.66.

By increasing the ionic strength from 0.01 to 0.1, by addition of lithium chloride at fixed concentrations of water and catalyst, the observed rate constant was doubled and varied according to the law: $\log k_I = a + b\sqrt{I}$, which is a relationship typical of secondary salt effects.

Effects of substituents in the benzene ring

There is a fairly good linear correlation between the logarithms of the relative rate constants, k_{rel} (relative to I, X = H) and the Hammett σ values of the substituents in the benzene ring. Based on the catalytic rate constants for catalysis by undissociated acid, the slope in Fig. 7 gives a ρ-value of -1.2 ± 0.1. The comparable value of ρ for the uncatalyzed reaction is -1.0 ± 0.05 (Fig. 7). Thus electron-donating substituents accelerate the reaction. In calculating ρ, the compounds with X = *m*-CH_3 and *m*-OCH_3 were disregarded since the logarithm of their rate constants deviated considerably from the straight line.

The enthalpies and entropies of activation of three compounds of the series were calculated for the acid catalyzed reaction. They are shown in Table 1, where the catalytic constants (k_{AcOH}) and relative rates (k_{rel}) have also been included.

The characteristic features of the process are the high, negative values of the entropy of activation and the low enthalpies of activation. It is hard to conclude from these results that the reaction is enthalpy-controlled. The smallness of the temperature coefficient of the rate, along with the high values for the rate constants will encumber the numerical results with comparatively large errors. The practically constant value for the entropy of activation would, however, suggest an enthalpy control of the reaction.

On the other hand, in the uncatalyzed reaction, when the substituents are made more electron withdrawing, both the enthalpy and entropy of activation decrease with decreasing rate. The effect of the unfavourable change in entropy on passing from the substrate to the transition state, on the free energy of activation, $\Delta G^{\neq}$, is clearly larger than that of the enthalpy change, as is seen from the last column of Table 2.

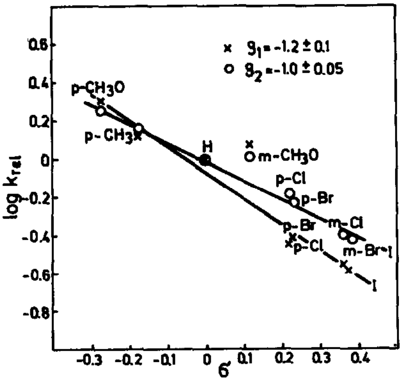


Fig. 7. Plot of $\log k_{rel}$ vs σ for solvolysis of $(Me_2Si)_3O_2NC_6H_4X$ in aqueous methanol, $[H_2O]$ 0.56 *M*; $I = 0.02$; *T* 25°C. ×, catalysed reaction (AcOH-AcONa), $k_{rel} = k^X_{AcOH}/k^H_{AcOH}$; ○, uncatalysed reaction, $k_{rel} = k^X_I/k^H_I$.

TABLE 1

REACTIVITIES OF *N*-ARYLCYCLOSILAZOXANES, $(Me_2Si)_3O_2NC_6H_4X$ IN CATALYSED SOLVOLYSIS IN AQUEOUS METHANOL [a]

X	T (°C)	$10^2 k_{AcOH}$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k_{rel} = k^X_{AcOH}/k^H_{AcOH}$	$\Delta H^{\neq}$ ($kcal\ mol^{-1}$) [$kJ\ mol^{-1}$]	$\Delta S^{\neq}$ (e.u.) [$kJ\ mol^{-1}\ deg^{-1}$]
H	25	1.08 ±0.02	1	6.0±1.4	−46.5±4.4
	35	2.40 ±0.03		[25.8±6]	[−0.195±0.02]
	45	2.75 ±0.02			
	55	2.93 ±0.03			
p-CH_3	25	1.40 ±0.1	1.30	6.7±0.8	−44.5±2.5
	35	2.44 ±0.15		[27.9±3.2]	[−0.19±0.01]
	45	2.92 ±0.3			
	55	4.65 ±0.01			
p-Cl	25	0.40 ±0.05	0.37	8.0±0.8	−42.5±2.4
	35	0.77 ±0.05		[33.7±3.3]	[−0.18±0.01]
	45	1.07 ±0.03			
	55	1.37 ±0.02			
m-CH_3	25	2.033±0.07	1.88		
p-CH_3O	25	2.22 ±0.05	2.06		
m-CH_3O	25	1.43 ±0.05	1.32		
p-Br	25	0.428±0.01	0.396		
m-Br	25	0.33 ±0.01	0.31		
m-Cl	25	0.385±0.02	0.36		

[a] $[H_2O] = 0.56\ M$, AcOH–AcONa, $I = 0.02$.

TABLE 2

REACTIVITIES OF *N*-ARYLCYCLOSILAZOXANES, $(Me_2Si)_3O_2NC_6H_4X$ IN THE UNCATALYZED SOLVOLYSIS IN AQUEOUS METHANOL [a]

X	T (°C)	$10^4 k_1$ (s^{-1})	k_{rel}	$\Delta H^{\neq}$ [$kcal\ mol^{-1}$) [$kJ\ mol^{-1}$]	$\Delta S^{\neq}$ (e.u.) ($kJ\ mol^{-1}\ deg^{-1}$)	$\Delta G^{\neq}$ ($kJ\ mol^{-1}$)
H	25	1.02	1	9.0±1.0	−47±4	98±5
	35	1.70		[37.5±5]	[−0.196±0.02]	
	45	2.534				
p-CH_3	25	1.408	1.38	12.0±0.7	−36±2	97±3
	35	2.85		[49.8±3]	[−0.15±0.01]	
	45	4.634				
m-CH_3	25	1.42	1.39			
p-CH_3O	25	1.817	1.78			
m-CH_3O	25	1.06	1.04			
p-Cl	25	0.665	0.65			
m-Cl	25	0.408	0.40	4.0±0.3	−66±1	101±1
	35	0.502		[15.6±1]	[−0.28±0.003]	
	45	0.618				
p-Br	25	0.608	0.60			
m-Br	25	0.390	0.38			

[a] $[H_2O] = 0.56\ M$, $I = 0.02$.

Solvent isotope effect

When the methanolysis of I (X = H) was carried out in a deuterated medium (CH_3OD–D_2O; CH_3COOD–CH_3COONa) the rate was found to be slightly enhanced, yielding the factor

$k_H/k_D = k_{AcOH}/k_{AcOD} = 0.87$

Mechanism of solvolysis of N-arylcyclosilazoxanes

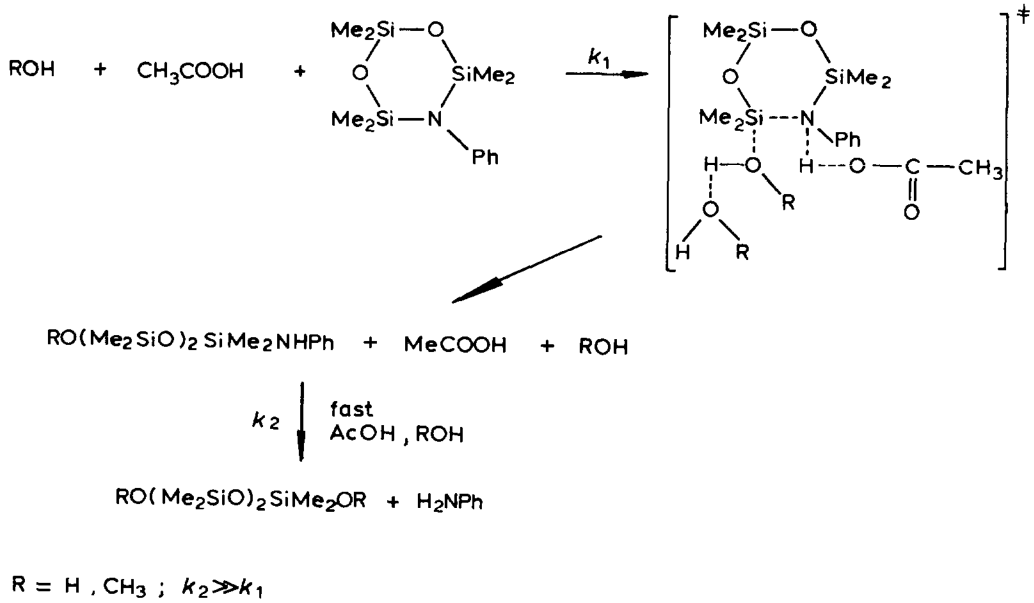
The solvolysis of the silazane bond in the cyclic silazoxanes can be represented as a system of two consecutive reactions. The first one, involving opening of the ring is considerably slower than the cleavage of the Si–N bond in the linear compound formed, which contains a terminal, secondary amino group (see scheme below). The rates of solvolysis of similar compounds, e.g. *N*-triethylsilylaniline in pure methanol, ethanol and isopropanol have been found to be too high to be measured by classical methods [4]. The rates, activation parameters and the subsequent discussion of the mechanism, therefore, refer to the first, slow step involving the elementary cleavage of a single Si–N bond in the ring compound.

The solvolytic cleavage of the Si–N bond takes place in a weakly acidic medium and is promoted by three catalytic processes: (1) catalysis by oxonium ions, (2) catalysis by undissociated acid molecules, and (3) catalysis by solvent molecules. The established general acid catalysis would suggest a proton transfer in the slow step of the reaction.

Examination of the Hammett relationship shows that the amount of positive charge on nitrogen is larger in the transition state relative to the ground state, which is consistent with the necessity for electrophilic assistance, achieved by protonation of nitrogen. Low absolute values of the reaction constant, ρ, which are nearly equal for the catalysed and "spontaneous" reactions, would suggest a similarity of mechanisms in both cases, but do not allow an unequivocal estimation of the degree of protonation of nitrogen in the transition state, since they can either result from a small degree of proton transfer to nitrogen or from the neutralization of charge brought about by a weakening of the silicon–nitrogen bond.

The large entropy loss in the process of activation is consistent with a mechanism in which the transition state is built up of several, previously independent, species. This will produce a substantial stiffening of the structure and separation of charge, which, in turn, will bring about considerable orientation of the solvent molecules. These features of the reaction are characteristic of a synchronous mechanism with possible involvement of a cyclic transition state. In particular, the low energies of activation can be related to a strong solvation of the transition state (the negative energy of solvation will act to reduce the overall energy of activation).

The reverse and near-unity kinetic isotope effect is not inconsistent with the involvement of a proton transfer in the slow step. It also suggests a highly unsymmetrical structure for the transition state; however, it does not allow differentiation between a reagent-like and product-like structure for the transition state, since in both cases a primary isotope effect close to unity would be expected. The enhancement of rate in a deuterated medium is symptomatic of the prevalence of secondary isotope effects. These can be related to the attack of the nucleophile on silicon and are dependent upon the extent of formation of the new silicon–oxygen bond. On the other hand, the overall isotope effect will be related to the necessity of desolvation of the attacking alcohol molecule and of the catalysing acid. The former effect would be expected to be close to unity if the new bond is not yet fully formed in the transition state. The magnitude of the latter is harder to estimate but would also be expected to reduce the k_H/k_D factor, which, assuming the primary isotope effect to be close to unity, would yield an overall effect close to the experimental value.



Proton-transfer to atoms of electronegative elements such as nitrogen or oxygen are usually fast and diffusion-controlled in the thermodynamically favoured direction. However, reducing the basicity of nitrogen, as in the present case, by $(p\text{–}d)\pi$ to the two silicon atoms can result in lowering the rate of proton-transfer to the extent of making it comparable to that of the slow nucleophilic substitution step. Thus a synchronous mechanism, as shown in the scheme, involving simultaneous nucleophilic attack on silicon by a solvent molecule and proton-transfer from the acid to nitrogen will be consistent with most of the experimental facts. In the light of the present results the transition state would seem to be rather reagent-like but more precise determination of the extent of formation of new bonds and breaking of the old ones will necessitate further experiments, which is the intention of the authors.

Comment on the role of water

The acceleration of both acid-catalyzed and "spontaneous" reactions by the addition of such an amphiprotic agent as water can result either from its proton donating role in the electrophilic assistance to the leaving group or from its part in the nucleophilic attack on silicon. The order in water, not much less than unity, seems to allow for only one of these factors. Considering the presence of products of hydrolysis in the reaction mixture this factor is the nucleophilic attack on silicon, in which water competes with the alcohol.

The role of water in the electrophilic assistance process will be suppressed by the

TABLE 3

PROPERTIES AND ANALYSES OF *N*-ARYL-1,1,3,3,5,5-HEXAMETHYLCYCLO-1,3,5-TRISILA-2-AZA-4,6-DIOXANES $(Me_2Si)_3O_2NC_6H_4X$

X	Yield (%)	M.p. (°C)	Elemental analysis (%) (Found (calcd.))					Molecular weight		Chemical shifts, δ ppm in ^1H NMR spectra (solvent CCl_4, internal standard CH_2Cl_2)				
			C	H	N	Si	Cl Br	Calc.	Found[a]	$-OSi(CH_3)_2N$	$-OSi(CH_3)_2O$	X	C_6H_4	λ[b] (nm)
H [16]	31	80	48.07	7.81	4.83	28.17	–	297.6	300	0.068 s(12H)	0.208 s(6H)	–	7.2 m (5H)	250
			(48.43)	(7.79)	(4.71)	(28.32)								
p-CH_3	35	79–80	49.49	8.10	4.53	27.41	–	311.6	320	0.15 s (12H)	0.28 s (6H)	2.38 s (3H)	7q (4H)	253
			(50.11)	(8.09)	(4.50)	(27.04)	–							
m-CH_3	30	81–83	49.55	8.09	4.46	27.09	–	311.6	304	0.088s (12H)	0.21 s (6H)	2.34 s (3H)	6.8m (4H)	253
			(50.11)	(8.09)	(4.50)	(27.04)	–							
p-CH_3O	40	74	47.80	7.65	4.23)	26.04	–	327.6	335	0.013s (12H)	0.16 s (6H)	3.75s(3H)	6.8m (4H)	250
			(47.66)	(7.69)	(4.28)	(25.72)	–							
m-CH_3O	25	56	47.83	7.81	4.64	25.72	–	327.6	310	0.013s (12H)	0.14 s (6H)	3.73s(3H)	6.8m (4H)	250
			(47.66)	(7.69)	(4.28)	(25.72)	–							
p-Cl	25	69–71	43.44	6.64	4.23	25.34	10.71	332	337	0.05 s (12H)	0.17 s (6H)	–	7.0m (4H)	263
			(43.41)	(6.68)	(4.22)	(25.38)	(10.68)							
m-Cl	20	88–89	43.31	6.80	4.52	24.81	10.60	332	333	0.013s (12H)	0.14 s (6H)	–	7.1m (4H)	256
			(43.41)	(6.68)	(4.22)	(25.38)	(10.68)							
p-Br	20	47	38.45	5.72	3.80	21.73	21.74	376.5	380	0.08s (12H)	0.2 s (6H)	–	7.1m (4H)	263
			(38.28)	(5.89)	(3.72)	(22.38)	(21.23)							
m-Br	10	63–65	38.30	6.20	3.70	21.98	21.00	376.5	370	0.04s (12H)	0.16s (6H)	–	7 m (4H)	253
			(38.28)	(5.89)	(3.72)	(22.38)	(21.23)							

[a] Osmometric (Hewlett-Packard 302 B). [b] Wavelength, at which UV absorptions were recorded in kinetic runs.

contribution of the stronger acid present. At very low concentrations of water, methanol is the sole effective nucleophile, as evidenced by the zero-order in water.

Experimental

All *N*-arylcyclosilazoxanes were prepared in a similar way to that used previously for synthesizing the parent compound *N*-phenyl-1,1,3,3,5,5-hexamethylcyclo-1,3,5-trisila-2-aza-4,6-dioxane [16]. They were purified by repeated sublimation and stored in evacuated vessels. Their yields, elemental analyses, physical properties and spectroscopic data are given in Table 3. For comments on the low yields see [16].

Analytical grade acetic acid was distilled from chromium oxide, Cr_2O_3; analytical grade sodium acetate and lithium chloride were dried at 100°C on a vacuum line and stored in vacuo. Methanol was dried by the standard method of distilling from magnesium methanolate and redistilling from a small amount of trinitrobenzoic acid through an adiabatic column, with glass filling, of 0.5 m length.

Deuterated acetic acid was prepared by hydrolysis of acetic anhydride with a less than stoichiometric amount of deuterium oxide. The isotopic purity of the CH_3COOD and CH_3OD was checked by ^1H NMR.

Rate measurements

Samples of stock solutions of acetic acid, sodium acetate and lithium chloride in anhydrous methanol were mixed in a volumetric flask in calculated proportions and diluted with methanol containing fixed amounts of water to obtain the desired concentrations. After adding a weighed amount of substrate to the solution at the desired temperature, a sample was transferred to a vapour-tight, thermostatted spectrometric cell. A Specord UV-VIS spectrophotometer was used for all kinetic runs. Changes in the UV absorption at selected wavelength (Table 3) were recorded to 90% conversion. The observed rate constants, k_I, were calculated by the Guggenheim method and least squares regression analysis. The error in k_I was within ±5% to ±10% and all the data presented are averages of a minimum of 3 determinations. The partial catalytic constants were calculated by least-squares using the equation: $k_I = k_0 + k_{AcOH}[AcOH] + k'_{R\overset{+}{O}H_2}[AcOH]/[AcONa]$. All the errors were estimated in the form of standard deviations. The activation parameters were obtained by using the Eyring equation.

Chromatographic analyses were performed on a JEOL gas liquid chromatograph with a flame ionization detector and an Takeda Riken TR 2215 A integrator; using a 2 m × 4 mm column, 10% OV-101 on Varaport 30/100 (120 mesh), programmed temperature, 50 → 280°C at 10°/min, with nitrogen, hydrogen as the carrier gas.

Mass spectra were recorded at 70 eV on a mass spectrometer LKB 9000, coupled to a gas chromatograph, ion source temperature 290°C. The IR spectra were taken on a Pye Unicam SP 1200 spectrometer in KBr. The ^1H NMR spectra were recorded on a Tesla BS 487 C (80 MHz) or a JEOL C-60 ML.

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References

1 R. Fessenden and J. Fessenden, Chem. Rev., 61 (1961) 361.
2 S.H. Langer, S. Connell and J. Wender, J. Org. Chem., 23 (1958) 50.
3 R. Fessenden and D. Crowe, J. Org. Chem., 25 (1960) 598.
4 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organomet. Chem., 25 (1970) 57.
5 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organomet. Chem., 43 (1972) 265.
6 K.A. Andrianov, M. Kustuj, P.L. Prichod'ko, J. Hajduk, V.M. Kopylow, Zh. S. Syrcova and M.I. Shkolnik, Zh. Obshch. Khim., 47 (1977) 600.
7 M. Ali, C. Eaborn and D.R.M. Walton, J. Organomet. Chem., 78 (1974) 83.
8 B. Bøe, C. Eaborn and D.R.M. Walton, J. Organomet. Chem., 82 (1974) 17.
9 W. Giessler, Doctoral Dissertation, University of Köln, 1963.
10 E. Frainnet, A. Bazouin and R. Calas, C.R. Acad. Sci. Paris, 257 (1963) 1304.
11 J.F. Klebe and J.B. Bush, Ist International Symposium on Organosilicon Chemistry, Prague, 1965, Conference Abstr., p. 328.
12 Z. Lasocki and J. Kowalski, J. Organomet. Chem., 152 (1978) 45.
13 E.P. Lebedev, V.O. Reikhsfeld, Zh. Obshch. Khim., 40 (1970) 2052.
14 E.P. Lebedev, V.O. Reikhsfeld, Zh. Obshch. Khim., 40 (1970) 2056.
15 E.P. Lebedev, V.O. Reikhsfeld and I.E. Saratov, Khim. i Prakt. Primen. Kremnii i Fosfororg. Soedin., (1977) 96. Ref. Zh. Khim., 16B (1978) 1229.
16 Z. Lasocki and M. Witekowa, Synth. React. Inorg. Met.-Org. Chem., 4 (1974) 231.
17 Z. Lasocki and M. Witekowa, J. Macromol. Sci., Chem., A 11 (1977) 457.
18 T. Shedlovsky and R.L. Kay, J. Phys. Chem., 60 (1956) 155.
19 R.L. Showen in A. Streitwieser Jr. and R.W. Taft (Eds.), Progress in Physical Organic Chemistry, Vol. IX, Wiley, New York, 1972.