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Rate studies of the acid-catalyzed solvolysis of eight-membered cyclosilazoxanes

Zygmunt Lasocki * and Małgorzata Witekowa
Institute of Polymers, Technical University, 90-924 Łódź (Poland)

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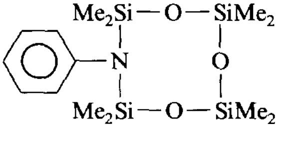
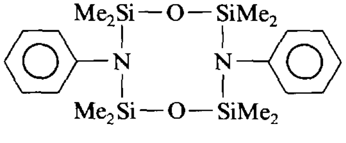
Abstract

The solvolysis of *N*-phenyl-1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2-aza-4,6,8-trioxacyclooctane (I) and *N,N'*-diphenyl-1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2,6-diaza-4,8-dioxacyclooctane (II) in methanol/water in the presence of an acetate buffer is a pseudo-first-order process, subject to general acid-catalysis. The catalytic rate constants have been determined spectrophotometrically for the solvolysis of I. The ring cleavage is slower than that of analogous six-membered cyclosilazoxanes, but the catalytic mode and the solvent isotope effect indicate a close mechanistic similarity between the solvolyses of six- and eight-membered rings

Introduction

Kinetic studies of the reactivity of the silicon-nitrogen bond in two series of cyclic six-membered silazoxanes [1,2] have now been extended to reactions of eight-membered rings in order to explore the effect of increasing the size of the ring on the rate and mechanism of the reaction. Detailed measurements were made for the heterolysis of compound I containing one silazane system in the ring. Rates were also determined for compound II, which has alternating silazane and siloxane bonds in the molecule.


(I)


(II)

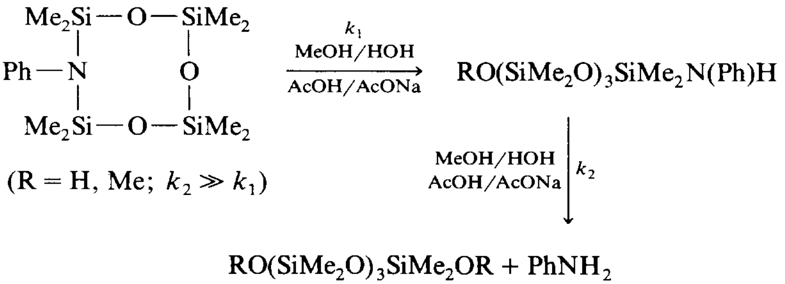
As in the case of six-membered ring compounds [3,4], the silazoxanes I and II have also been used as monomers for the synthesis of thermostable linear polysilazoxanes by anionic polymerization [5].

Evidence was previously presented to show that in weakly acidified aqueous-methanolic media the six-membered cyclosilazoxanes undergo ring opening with cleavage of the silicon–nitrogen bond. The mechanism involves nucleophilic attack by the solvent on silicon and is electrophilically assisted by synchronous proton transfer from the catalyzing acid to nitrogen [1,2].

In order to find if a similar mechanism operates for the eight-membered silazoxane system and also to permit quantitative comparison of the kinetic data, the reaction medium (aqueous methanol and acetate buffer) and conditions (constant concentration of water and ionic strength) used for the six-membered rings were again employed. The progress of the reaction was monitored by UV spectroscopy by observing the absorption change at a wavelength selected from the benzenoid band of aniline so as to give the largest difference in molar extinction coefficient between the product (aniline) and substrate.

Results and discussion

Chromatographic analysis showed that the silicon–nitrogen bond was cleaved and the siloxane system fully preserved under the reaction conditions used. The solvolysis of silazane in the eight-membered ring proceeds in the same way as that of the six-membered compounds and, so can be represented as a system of two consecutive reactions. The first of these, ring opening, is considerably slower than the next one, the silicon–nitrogen bond cleavage in the molecule of the linear intermediate, which contains a secondary amino group [1]. Thus the kinetic data and the subsequent discussion of mechanism refer to the elementary cleavage of the Si–N bond in the ring.



At a fixed concentration of buffer and constant ionic strength the reaction is pseudo-first-order in cyclosilazoxane. First-order plots were obtained up to high (90%) conversion, and the rate constant k_1 was found to be independent of the initial concentration of the cyclosilazoxane (Fig. 1). Overall first-order kinetics were also established.

The features of the catalyzed process do not differ from those observed for the reaction of the six-membered cyclosilazoxanes [1,2]. The observed rate constant k_1 is linearly related to the concentration of acetic acid (0.01–0.15 M) at a fixed buffer ratio and constant ionic strength. From the slope of the straight line plots the partial catalytic constant k_{AcOH} for the undissociated acid was determined. Similarly, good straight line plots with slope $k'_{\mathrm{R\overset{+}{O}H_2}}$ were obtained for the relationship between k_1 and the buffer ratio (5 to 50) at a constant concentration of acetic acid. The apparent catalytic rate constant is related to the actual value by the equation: $k'_{\mathrm{R\overset{+}{O}H_2}} = k_{\mathrm{R\overset{+}{O}H_2}} \cdot K_{\mathrm{AcOH}}$ (K_{AcOH}: dissociation constant of acetic acid in aqueous methanol). Thus, the system is subject to general acid catalysis.

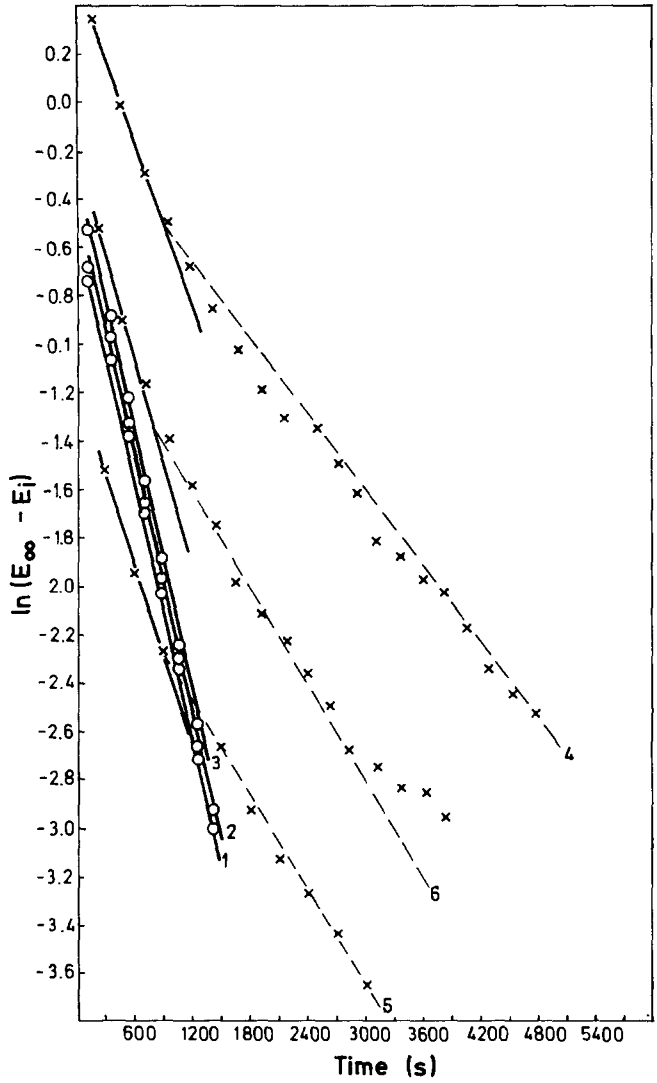


Fig. 1. First order plots for the solvolysis of *N*-phenylcyclosilazoxane (I) (1–3) and *N*,*N*′-diphenylcyclosilazoxane (II) (4–6) in aqueous methanol, [H_2O] 0.56 *M*; $I = 0.02$; *T* 25 °C; [AcOH]/[AcONa] = 10. Concentrations (*M*): [AcOH] 0.05, 1, c_0 3.15×10^{-4}; 2, 3.29×10^{-4}; 3, 3.93×10^{-4}; 4, [AcOH] 0.025, c_0 2.5×10^{-4}; 5, [AcOH] 0.025, c_0 5.4×10^{-5}; 6, [AcOH] 0.05, c_0 1.39×10^{-4}; c_0 = initial concentration of silazoxane.

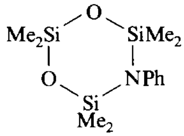
The values of the partial catalytic rate constants for the solvolysis of cyclosilazoxane I are listed in Table 1, together with those for the six-membered cyclosilazoxanes III [1] and IV [2] for comparison. The values of the enthalpies and entropies of activation or the acid catalyzed reaction are also shown. The kinetic data for the reaction of compound I suggest a close similarity with the mechanism previously suggested for solvolysis of III and IV. This includes a slow proton transfer from the catalyzing acid to the substrate, probably synchronous with the nucleophilic attack by the solvent molecule on silicon. The low energy of activation as well as the

Table 1

Solvolysis of cyclosilazoxanes I, III [a] and IV [b] in methanol/water/acetate buffer

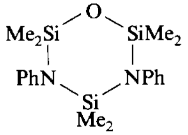
T (°C)		k_{AcOH} ($\times 10^{-2}$) (dm^3 mol^{-1} s^{-1})	$k'^{+}_{ROH_2}$ ($\times 10^{-4}$) (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1}) [kJ mol^{-1}]	$\Delta S^{\ddagger}$ (e.u.) [kJ mol^{-1} deg^{-1}]	k_{AcOH}/k_{AcOD}
I	25	0.542 ± 0.03	1.52 ± 0.1	5.1 ± 1.1	−43.05 ± 5	0.4
	35	0.635 ± 0.03		[21.3 ± 4.6]	[−0.18 ± 0.02]	
	45	0.935 ± 0.02				
III [1]	25	1.07 ± 0.02	1.92 ± 0.1	5.0 ± 1.4	−46.5 ± 4.4	0.87
				[25.8 ± 6]	[−0.195 ± 0.02]	
IV [2]	25	6.9 ± 0.1	6.5 ± 0.2	3.8 ± 1.4	−51 ± 5	0.96
				[15.8 ± 6]	[−0.21 ± 0.02]	

[a]



(III)

[b]



(IV)

strongly negative entropy of activation are typical of a bimolecular reaction concerted with electrophilic assistance by the catalyzing acid. The transition state is characterized by a "rigid" structure, composed of three previously independent species, and by considerable separation of charge, which causes substantial orientation of solvent molecules.

The rate was found to be enhanced in a deuterated medium (CH_3OD–D_2O; CH_3COOD–CH_3COONa), and the ratio k_H/k_D was 0.4 (for the acid catalyzed reaction). This inverse kinetic solvent isotope effect is not fully consistent with the accepted notion based on experimental data [6] that for a slow rate determining proton transfer the value of k_H/k_D should be higher or not much less than unity. However, if a highly unsymmetrical transition state is assumed, which will make the primary isotope effect close to unity, the low value of the solvent isotope effect can result from the predominance of secondary isotope effects [7]. These can be related to the extent of formation of the new silicon–oxygen bond. By analogy to the mechanism of solvolysis of six-membered silazoxanes we suggest a reagent-like structure for the transition state with a small degree of proton tranfer.

Water accelerates the solvolysis of I (Table 2) and the order with respect to water is 0.77. The role of water was discussed previously [1] and similar conclusions can be reached in the present case.

The investigation of the reactivity of the Si–N bond in *N*-phenylcyclosilazoxanes was extended to include the measurement of the pseudo-first-order rate constant for

Table 2

Effect of water concentration on the observed rate constants in solvolysis of $(Me_2SiO)_3Me_2SiNPh$ (I) in aqueous methanol [a]

$[H_2O]$ (M)	0.111	0.278	0.389	0.556	0.833	1.11
$10^3 k_1$ (s^{-1})	0.668	1.05	1.27	1.58	2.26	2.58

[a] [AcOH] = 0.025 M, [AcONa] = 0.0025 M, $I = 0.02$, $T = 25$ °C.

Table 3

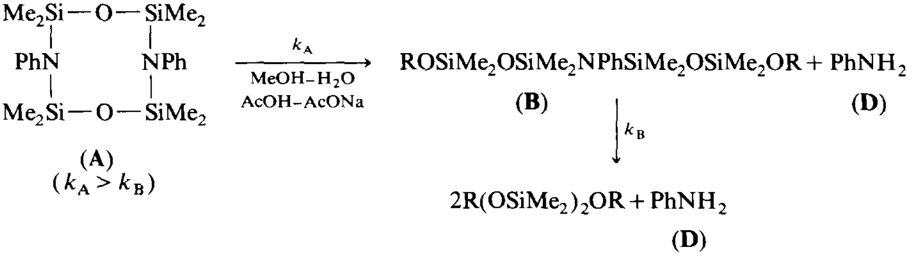
Experimental pseudo-first-order rate constants in the solvolysis of six- (III and IV) and eight membered (I and II) cyclosilazoxanes in methanol/water/acetate buffer [a]

	[AcOH] (M)	10^4Co (M)	10^3k_1 (s^{-1})		[AcOH] (M)	10^4Co (M)	$10^3k'_A$ (s^{-1})	10^3k_A (s^{-1})
I	0.025	3.03	2.33	II	0.025	2.5	1.31	
	0.025	4.15	2.47		0.025	4.1	1.30	
	0.05	1.45	2.83		0.025	5.4	1.23	
	0.05	2.6	2.70		0.05	1.39	1.37	
	0.05	5.7	2.88		0.05	3.5	1.36	
III	0.025	2.7	2.13	IV	0.025	1.4	3.1	8.45
	0.05	4.5	2.40		0.05	3.0	4.05	11.2

[a] $[H_2O] = 0.56$ M, $[AcOH]/[AcONa] = 10$, $I = 0.02$, $T = 25\,°C$.

the solvolysis of cyclosilazoxane (II) containing two symmetrically distributed silazane bonds in the molecule. This compound has been found to have the highest stability under the severe conditions used in anionic polymerization: the ring was not cleaved at 180 °C in the presence of the initiator and activators [5].

In aqueous methanol containing an acetate buffer the silazane linkage is cleaved and the kinetics of solvolysis are similar to those previously established for the six-membered ring compound IV [2]. The reaction involves two consecutive pseudo-first-order reactions:



From the initial slope of the first-order plots in Fig. 1 the apparent rate constant k'_A of the cleavage of cyclosilazoxane II was determined; k'_A is related to the real constant k_A by: $k'_A = k_A(\epsilon_D + \epsilon_B + \epsilon_A)/(2\epsilon_D - \epsilon_A)$ [2] ($\epsilon_{A,B,D}$-molar extinction coefficients of substrate **A**, intermediate **B**, and product **D**).

As can be seen from Tables 1 and 3 there is no substantial difference between the reactivities of the six- (III) and eight-membered (I) silazoxane rings containing one silazane bond; the effects of the catalytic processes are also similar. In the series of compounds containing two silazane bonds the eight-membered ring (II) is three times less reactive than the six-membered one (IV), and this is probably related to lower strain in structure II. The high reactivity of IV (compare k_A for IV with k_1 for I and III) can be taken as indirect evidence that the most likely site for the nucleophilic attack resulting in ring opening is the silicon atom situated between two nitrogens, which seems to be the most electrophilic centre in the molecule.

Experimental

Aniline, triethylamine, and the solvents were purified and carefully dried by the procedures described in Ref. 8. 1,7-Dichlorooctamethyltetrasiloxane and 1,3-dichlorotetramethyldisiloxane were prepared by partial hydrolysis of dichlorodimethylsilane [9] and fractionated through an efficient distillation column.

N-*Phenyl-1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2-aza-4,6,8-trioxacyclooctane*

Aniline (0.46 mol) was added during 1 h to a stirred solution of 1,7-dichlorooctamethyltetrasiloxane (0.45 mol) and triethylamine (0.92 mol) in *N,N*-dimethylformamide (DMF, 400 ml). Stirring was continued for 4 h at room temperature. The precipitated triethylamine hydrochloride was filtered off and washed with DMF, and the filtrate then evaporated. The residual liquid was fractionated under reduced pressure in a nitrogen atmosphere and the product collected at b.p. 87 °C/0.6 Torr, n_D^{20} 1.463, yield 20% (Found: C, 43.98; H, 7.75; N, 3.56; Si, 29.52. $C_{14}H_{29}NO_3Si_4$ calc.: C, 45.28; H, 7.82; N, 3.77; Si, 30.19%). IR Specord 75 IR (neat, cm^{-1}): Si–N–Si 920, 960; Si–O–Si 1020, 1060; $C{=}C_{ar}$ 1400, 1480, 1590, 1640; C_{ar}–N 1250. ^1H NMR (Tesla BS 487C, 80 MHz, CCl_4; CH_2Cl_2 as int. standard): δ 0.10 (s, 12H); 0.20 (s, 12H); 7.1 (m, 5H). ^{29}Si NMR (Bruker 300, $C_6H_5CD_3$ as solvent and int. standard): δ −13.29 (s, 2Si); −21.64 (s, 2Si).

N,N′-*Diphenyl-1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasila-2,6-diaza-4,8-dioxacyclooctane*

In a similar procedure, after addition of aniline (0.5 mol) to a solution of 1,3-dichlorotetramethyldisiloxane (0.5 mol) and triethylamine (1 mol) in DMF (400 ml) and a further 4 h stirring followed by filtration, the filtrate was cooled to −20 °C. The precipitate which separated was treated with ether, the undissolved solid was filtered off, and the residual solution evaporated to dryness. The residual solid (yield 31%) was recrystallized from ether yielding material of m.p. 58–59 °C (Found: C, 53.68; H, 7.88; N, 5.94; Si, 24.98. $C_{20}H_{34}N_2O_2Si_4$ calc.: C, 53.81; H, 7.62; N, 6.28; Si, 25.11%). IR (Nujol, cm^{-1}): Si–N–Si 900, 980; Si–O–Si 1020, 1050; $C{=}C_{ar}$ 1400, 1450, 1590; C_{ar}–N 1250. ^1H NMR (in CCl_4; CH_2Cl_2 as int. standard): δ 0.20 s (24H), 7.15 m (10H). ^{29}Si NMR (in $C_6D_5CD_3$ as solvent and int. standard): δ −9.0 (s).

Rate measurements

All the reagents, solvents, catalysts and deuterated compounds were prepared, purified, and dried as described previously [1]. The cyclosilazoxanes were redistilled or recrystallized before each run and stored *in vacuo*.

Table 4

Effect of acetate buffer concentration on the observed rate constants in solvolysis of $(Me_2SiO)_3Me_2SiNPh$ (I) in aqueous methanol and deuteromethanol [a]

[AcOH]	(M)	0.01	0.05	0.07	0.1	0.12	0.15	0.05	0.05	0.05	0.05
[AcONa]	(M)	0.001	0.005	0.007	0.01	0.012	0.015	0.01	0.0033	0.00166	0.001
$10^3 k_{1(H)}$	s^{-1}	1.66	1.825	1.998	2.17	2.30	2.40	1.17	2.76	4.97	7.99
[AcOD]	(M)	0.01	0.02	0.04	0.06	0.09	0.12				
[AcONa]	(M)	0.001	0.002	0.004	0.006	0.009	0.012				
$10^3 k_{1(D)}$	(s^{-1})	2.28	2.49	2.76	2.96	3.53	3.77				

[a] $[H_2O]([D_2O]) = 0.28$ M, $I = 0.02$, $T = 25$ °C.

The method described previously [1] was used. The change in UV absorption (E) in vapour-tight thermostatted cells was recorded at wavelength λ of 250 nm. (Spectrometer UV-Vis, Carl Zeiss, Jena). The observed pseudo-first-order rate constant k_1 for compound I was calculated by the Guggenheim method and least-squares regression analysis. The apparent pseudo-first-order rate constant k'_A for the first stage of solvolysis of compound II was determined by use of the equation $2.303 \log(E_\infty - E_i) = k'_A t + c$, where E_i is the absorption at time t and E_∞ that after 24 h. All data are averages of at least 3 determinations, and the uncertainties in k_1 and k'_A are between $\pm 5\%$ and $\pm 10\%$. The partial catalytic constants for I were calculated from data in Table 4, as described previously [1]. The activation parameters were obtained by using the Eyring equation.

Acknowledgements

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