TABLE I
RATE DATA FOR THE Ni(II)–ACETONITRILE
EXCHANGE REACTION

Quantity	Value
$1/\tau_M$, sec^{-1} at 25°	$(2.8 \pm 0.5) \times 10^3$
$\Delta H^{\ddagger}$, kcal/mole	11.7 ± 1.0
$\Delta S^{\ddagger}$, cal/deg	-3.6 ± 1.0
A/h, cps^a	$-(8.1 \pm 0.5) \times 10^5$

^{a} Calculated assuming $\mu_{eff} = 3.15$ BM.[8]

If the chemical shift between bound and free aceto-nitrile is not too small ($\Delta\omega_M{}^2 \gg 1/T_{2M}\tau_M$) the term in T_{2M} can be neglected and the value of τ_M can be derived if $\Delta\omega_M$ is known from independent measurements. In Figure 2 a plot of $\Delta\omega_M$ *vs.* $1/T$ is given. At the lowest temperatures, the exchange is quite slow and has little effect on the spectrum. In this region (which is not
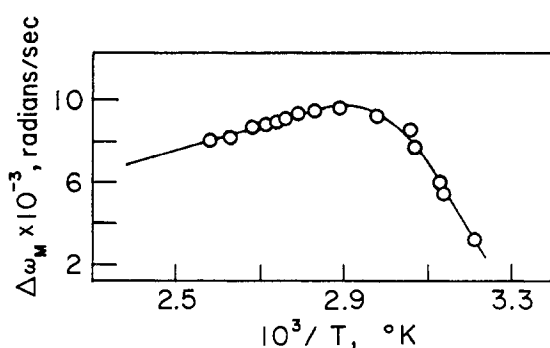

Figure 2.—Temperature dependence of $\Delta\omega_M$ for the protons in acetonitrile solutions of $Ni(CH_3CN)_6(ClO_4)_2$ at 56.4 Mc.

shown on the graph) there is zero chemical shift between the Ni(II) solutions and pure acetonitrile. The shift increases steeply at temperatures where the exchange rate becomes important, and in the limit of very fast chemical exchange it becomes linear with reciprocal temperature. In the latter region the part of the shift due to "contact" interaction is given by[9]

$$\frac{\Delta\omega_M}{\omega} = -\frac{A}{h}\frac{[S(S+1)]^{1/2}\mu_{eff}}{3kT\gamma_I} \quad (5)$$

where k is Boltzmann's constant, ω is the resonance frequency, γ_I is the magnetogyric ratio of the proton, and μ_{eff} and S refer to the Ni(II) ion. A value of the constant A/h calculated from the slope of the high-temperature region of Figure 2 is given in Table I. It is evident that additional terms contribute to the chemical shift; although $\Delta\omega_M$ is linear with $1/T$ in the high-temperature region, the extrapolated line does not pass through the origin as eq 5 would predict.

It is possible to compare the results of chemical-shift and line-width measurements at the higher temperatures. A value of $\Delta\omega_M$ can be calculated from the line-width data if the term in T_{2M} is neglected and τ_M is obtained by extrapolation from lower temperature. The chemical shift derived from this analysis at $1/T = 0.0029$ is 7.8×10^3 radians/sec, as compared with the value of 9.8×10^3 from direct measurement. Due to the

(9) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

long extrapolation involved, it is not clear whether the discrepancy between these numbers is a real effect. It is possible that this point will be cleared up by line-width studies on the ^{14}N nucleus.

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Aminolysis of α,ω-Dichlorosiloxanes[1]

BY L. W. BREED, M. E. WHITEHEAD, AND R. L. ELLIOTT

Recently, we reported the synthesis and properties of N-methylsiloxazanes, which were obtained in mixtures with α,ω-bis(methylamino)siloxanes when α,ω-dichloro-siloxanes in petroleum ether at 5–10° were treated with methylamine and the mixtures were refluxed.[2] In the absence of catalysts, the α,ω-bis(methylamino)-siloxanes were thermally stable and could readily be purified by distillation, but in the presence of ammonium sulfate they could be condensed to cyclic N-methyl-siloxazanes at 150–180°. It had been reported by others[3] that the α,ω-bis(methylamino)siloxanes were the sole product of the aminolysis reaction.

The differences in the nature of the products reported in these two publications can now be explained on the basis of a temperature effect. In subsequent studies of the synthesis of cyclic siloxazanes, we find that the linear bis(methylamino)siloxanes are the predominant products when the reaction mixtures are maintained below $-15°$, but cyclic N-methylsiloxazanes are the chief products when the reactions are carried out at 50° or above. Intermediate temperatures such as those reported in our earlier publication afford nearly equal amounts of the two products. A summary of typical experiments which illustrate this temperature effect is given in Table I.

Since the products of treating methylamine with α,ω-dichlorosiloxanes at low temperatures were re-fluxed before the mixtures were purified, the formation of substantial quantities of cyclic compounds at higher reaction temperature cannot be attributed to thermal condensation or to condensation catalyzed by the presence of the methylamine hydrochloride by-product. A more plausible explanation for cyclic compound

(1) This research was supported by the National Aeronautics and Space Administration under Contract NAS8-11338 and was monitored by the Materials Division, Propulsion and Vehicle Engineering Laboratory, George C. Marshall Space Flight Center.
(2) R. L. Elliott and L. W. Breed, *Inorg. Chem.*, **4**, 1455 (1965).
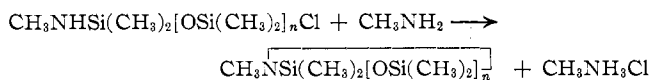(3) C. R. Krueger and E. G. Rochow, *ibid.*, **2**, 1295 (1963).

TABLE I

AMINOLYSIS PRODUCTS OF α,ω-DICHLOROSILOXANES

α,ω-Dichlorosiloxane	Mode of addn[a]	Temp, °C	Product distribution, %	
			Cyclic	Linear
1,3-Dichlorotetra-methyldisiloxane	A	5[b]	31	40
	A	50	62	8
	B	−30	c	82
1,5-Dichlorohexa-methyltrisiloxane	A	5[b]	43	33
	A	50	66	c
	A	25–50[d]	64	10
	A	−10	c	52
	B	−30	c	86
1,7-Dichloroocta-methyltetrasiloxane	A	55	61	c
	B	−15	76	c

[a] A, amine to siloxane; B, siloxane to amine. [b] Reference 2.
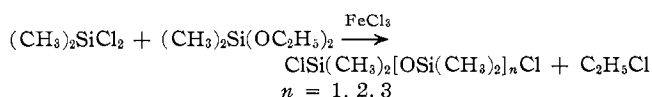[c] None isolated. [d] No temperature control.

formation at higher temperatures would be the greater probability for intramolecular condensation through enhanced chain mobility of the partially substituted α,ω-dichlorosiloxanes.

$$CH_3NHSi(CH_3)_2[OSi(CH_3)_2]_nCl + CH_3NH_2 \longrightarrow$$
$$\overline{CH_3NSi(CH_3)_2[OSi(CH_3)_2]_n} + CH_3NH_3Cl$$

The mode of addition can also favor the formation of one product or the other: Addition of the chlorosiloxane to the amine maintains a large excess of amine throughout the reaction and affords the highest conversions to the linear aminosiloxane; addition of the amine to the chlorosiloxane favors the formation of the partially-substituted chlorosiloxane which can cyclize. However, the identity of the product is determined by temperature. For example, when the same mode of addition is used in the conversion of 1,5-dichlorohexamethyltrisiloxane, 66% of the cyclic derivative is obtained at 50°, 52% of the linear derivative at −10°, and a mixture of 43% of the cyclic and 33% of the linear derivative at +5°.

Physical properties for these compounds are reported in Table II. Data for several of the compounds were obtained on materials of higher purity than those available earlier.

The α,ω-dichlorosiloxanes for these experiments were conveniently prepared by the equilibration of a 4:1 mole ratio mixture of dichlorodimethylsilane and diethoxydimethylsilane in the presence of ferric chloride. Such a procedure is far more convenient than the

$$(CH_3)_2SiCl_2 + (CH_3)_2Si(OC_2H_5)_2 \xrightarrow{FeCl_3}$$
$$ClSi(CH_3)_2[OSi(CH_3)_2]_nCl + C_2H_5Cl$$
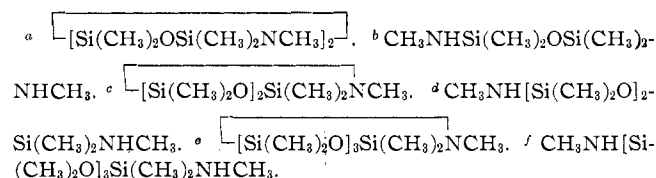$$n = 1, 2, 3$$

controlled hydrolysis of dichlorodimethylsilane solutions, and more applicable to the preparation of higher oligomers than the method described in our earlier publication for the preparation of 1,3-dichlorotetramethyldisiloxane.

Experimental Section

The following are experiments demonstrating preferred procedures for the compounds described in this paper. Nmr spectra (60

TABLE II

PHYSICAL PROPERTIES OF α,ω-BIS(METHYLAMINO)SILOXANES AND N-METHYLSILOXAZANES

Compound	Bp, °C	n^{20}D
Decamethyl-1,5-diaza-3,5-dioxa-2,4,6,8-tetrasilacyclooctane[a]	87–88 (5 mm) mp 27–28°	1.4321 (n^{30}D)
1,3-Bis(methylamino)tetramethyldisiloxane[b]	67–68 (20 mm)	1.4138
Heptamethyl-1-aza-2,4,6-trisilacyclohexane[c]	60–61 (17 mm)	1.4100
1,5-Bis(methylamino)hexamethyltrisiloxane[d]	97–98 (20 mm)	1.4102
Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane[e]	84–85 (8 mm)	1.4202
1,7-Bis(methylamino)octamethyltetrasiloxane[f]	114–115 (9 mm)	1.4100

[a] $\overline{[Si(CH_3)_2OSi(CH_3)_2NCH_3]_2}$. [b] $CH_3NHSi(CH_3)_2OSi(CH_3)_2$-NHCH_3. [c] $\overline{[Si(CH_3)_2O]_2Si(CH_3)_2NCH_3}$. [d] $CH_3NH[Si(CH_3)_2O]_2$-Si(CH_3)_2NHCH_3. [e] $\overline{[Si(CH_3)_2O]_3Si(CH_3)_2NCH_3}$. [f] $CH_3NH[Si(CH_3)_2O]_3Si(CH_3)_2NHCH_3$.

Mc) were obtained on approximately 10% solutions with cyclohexane as an internal standard. Elemental analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

α,ω-**Dichlorosiloxanes.**—After a mixture of 248 g (2 moles) of diethoxydimethylsilane, 1132 g (8 moles) of dichlorodimethylsilane, and 1.5 g of ferric chloride was heated at 85° for 7 hr, ethyl chloride was no longer evolved. Upon distillation, 514 g of dichlorodimethylsilane was recovered and 547 g of oligomers boiling between 25 and 140° (40 mm) was obtained. Fractional distillation of the oligomers gave the following compounds: 1,3-dichlorotetramethyldisiloxane, 287 g, bp 57–58° (40 mm), lit.[4] bp 41° (20 mm); 1,5-dichlorohexamethyltrisiloxane, 138 g, bp 94–96° (40 mm), lit.[4] bp 79° (20 mm); and 1,7-dichlorooctamethyltetrasiloxane, 23.6 g, bp 127–128° (41 mm), lit.[4] bp 111° (20 mm).

Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane.—Methylamine (50 ml) was condensed and subsequently distilled into a flask containing 40.2 g (0.11 mole) of 1,7-dichlorooctamethyltetrasiloxane in 200 ml of petroleum ether, bp 60–90°, which was heated to 50°. The reaction was exothermic, and external cooling was applied to the reaction vessel to maintain a constant temperature during the addition. The mixture was cooled and filtered, and the salts were washed with petroleum ether. After the solvent was distilled, fractional distillation gave 20.7 g (61%) of nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane, bp 84–85° (8 mm), n^{20}D 1.4202; nmr peaks (CCl$_4$) at τ 9.86 (12 H singlet, OSi(CH$_3$)$_2$N), τ 9.94 (12 H singlet, OSi(CH$_3$)$_2$O), and τ 7.50 (3 H singlet, NCH$_3$); and infrared absorption (neat liquid) at 905 and 1180 cm^{-1} (SiN).

Anal. Calcd for C$_9$H$_{27}$NO$_2$Si$_4$: C, 34.90; H, 8.79; N, 4.52; Si, 36.28. Found: C, 35.19; H, 8.54; N, 4.80; Si, 36.15.

1,7-Bis(methylamino)octamethyltetrasiloxane.—After 40.5 g (0.115 mole) of 1,7-dichlorooctamethyltetrasiloxane was added to 25 ml of methylamine in 100 ml of petroleum ether, bp 35–60°, which was maintained at −30° during the addition, the mixture was warmed to room temperature, refluxed 2 hr, and filtered, and the solvent was removed. Fractional distillation afforded 29.7 g. (76%) of 1,7-bis(methylamino)octamethyltetrasiloxane, bp 114–115° (9 mm), n^{20}D 1.4100°; nmr peaks at τ 9.92 (12 H singlet, OSi(CH$_3$)$_2$N), τ 9.94 (12 H singlet, OSi(CH$_3$)$_2$O), and τ 7.48 (6 H doublet, J = 6.5 cps, NHCH$_3$); and infrared absorption (neat liquid) at 3450 cm^{-1} (NH).

Anal. Calcd for C$_{10}$H$_{32}$N$_2$O$_3$Si$_4$: C, 35.24; H, 9.46; N, 8.22; Si, 32.97. Found: C, 35.06; H, 9.20; N, 7.98; Si, 32.74.

(4) W. Patnode and D. Wilcock, *J. Am. Chem. Soc.*, **76**, 1390 (1954).