Contribution from Monsanto Company Central Research Department,
St. Louis, Missouri, and the University of Pretoria, South Africa

Simultaneous Scrambling of Methoxyl, Dimethylamino, and Chloro Groups on Silicon

By JOHN R. VAN WAZER and SAREL NORVAL[1]

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Proton nuclear magnetic resonance has been used to investigate the molecular composition of the three-component liquid system $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$. The three completely mixed compounds $Si(OCH_3)_2[N(CH_3)_2]Cl$, $Si(OCH_3)[N(CH_3)_2]_2Cl$, and $Si(OCH_3)[N(CH_3)_2]Cl_2$ must maximize at the stoichiometry corresponding to their particular composition in the equilibrium mixtures. The observed maximum equilibrium amounts at 120° were about 35, 6, and 37% of the total Si, respectively, as compared to the statistically random value of 18.8%. Kinetic studies at these three compositions showed that the reaction between silicon tetrachloride and tetrakis(dimethylamino)silane as well as succeeding reactions between compounds of the type $SiCl_i[N(CH_3)_2]_{4-i}$ were 10^2–10^5 times faster at 38.5° than the subsequent reactions in which the methoxyl group was scrambled. In line with previous work on scrambling reactions, the kinetic runs were found to be complicated, with some of the molecular species going through a maximum as a function of time.

Although a considerable body of information[2-4] is now being built up on the equilibrium constants and the kinetics of redistribution reactions, there is only one[5] published paper in which an equilibrium study was made on the exchange of three different substituents on a given polyfunctional atom. Moreover, this previous paper dealt in a cursory fashion with the compound containing the three substituents. Studies of the simultaneous scrambling of more than two substituents are of particular interest in that they disclose the presence of the compound(s) in which more than two different monofunctional substituents are found and clarify the relations of these compounds with the more-often studied mixed structures based on two substituents.

In a previous study[3] published in this journal, we investigated the scrambling of methoxyl, dimethylamino, and chloro groups on silicon when these groups were taken two at a time, and the findings presented herein should be compared with those of this earlier paper. It is also of interest to relate this pair of studies to the investigation[4] in which methoxyl, dimethylamino, and chloro groups were scrambling two at a time on the methyl- and dimethylsilicon moieties. To our knowledge, there is no previous literature on the three mixed compounds $Si(OCH_3)_2[N(CH_3)_2]Cl$, $Si(OCH_3)[N(CH_3)_2]_2Cl$, and $Si(OCH_3)[N(CH_3)_2]Cl_2$.

Experimental

The reagents and general procedures which were described previously[3] were used in this study. Kinetic measurements were run at 38.5° and the equilibrium data correspond to 1 week at 120°. Pilot experiments indicated that equilibrium was achieved at this temperature in about 2 days.

The nuclear magnetic resonance (n.m.r.) chemical shifts as measured in this study agreed within 0.02 p.p.m. with the reported values[3] except for those of the compounds $Si(OCH_3)_4$, $Si(OCH_3)_3Cl$, and $Si(OCH_3)_2Cl_2$, which were 0.03 to 0.04 p.p.m. low. The proton n.m.r. chemical shifts (p.p.m.) which have not previously been reported are given below, where the first number refers to the resonance in the methoxyl region and the second to that in the dimethylamino region of the spectrum: $Si(OCH_3)_2[N(CH_3)_2]Cl$, −3.55, −2.53; $Si(OCH_3)[N(CH_3)_2]_2Cl$, −3.45, −2.53; $Si(OCH_3)[N(CH_3)_2]Cl_2$, −3.63, −2.58; and $Si(OCH_3)_3[N(CH_3)_2]$, −3.45, −2.52. In all cases, referencing was carried out by dissolving tetramethylsilane in the undiluted samples, and negative shifts were downfield.

In the methoxyl region of the n.m.r. spectrum, all of the observed resonances were completely resolved except those for $Si(OCH_3)_3[N(CH_3)_2]$ and $Si(OCH_3)[N(CH_3)_2]_2Cl$, which were separated by only 0.2 c.p.s. at 60 Mc. Except for a pair of lines lying 0.6 c.p.s. apart and three lines equally separated by 0.3 c.p.s., good resolution was also observed in the dimethylamino region of the spectrum. The poorly resolved pair of resonances corresponded to $Si(OCH_3)[N(CH_3)_2]Cl_2$ and $Si[N(CH_3)_2]_2Cl_2$, while the close-lying triplet was made up of the resonances for $Si(OCH_3)_2[N(CH_3)_2]Cl$, $Si(OCH_3)[N(CH_3)_2]_2Cl$, and $Si(OCH_3)_3[N(CH_3)_2]$. Because of the presence of two resonances (one in the methoxyl and the other in the dimethylamino spectral regions) for each compound except $Si(OCH_3)_4$, $Si[N(CH_3)_2]_4$, and $SiCl_4$, this poor resolution proved disadvantageous only in the case of the pair of compounds $Si(OCH_3)_3[N(CH_3)_2]$ and $Si(OCH_3)[N(CH_3)_2]_2Cl$, the sum of which was accurately measurable but could only be approximately apportioned between this pair of structures. It should also be remembered that the amount of $SiCl_4$ was necessarily determined by difference from the stoichiometry of the starting materials.

All area measurements were made with the integrator circuit of a Varian A-60 spectrometer. Since no $SiCl_4$ was found to be present in any of the equilibrium compositions, the precise amount of the poorly resolved pair, $Si(OCH_3)_3[N(CH_3)_2]$ and $Si(OCH_3)[N(CH_3)_2]_2Cl$, could be accurately determined from the material balance in these cases. Fortunately this difficultly analyzable pair of compounds did not show up together in the kinetic runs in which, by the way, the $SiCl_4$ was always found to disappear quickly.

Results and Conclusions

In the system $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$, there is a total of 15 possible compounds, as shown in

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[1] Abstracted from work done for a D.Sc. thesis of Sarel Norval in the Department of Inorganic and Analytical Chemistry of the University of Pretoria, South Africa.

[2] Recent papers on the scrambling of a pair of monofunctional substituents on a polyfunctional atom are J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964); K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964); H. K. Hofmeister and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **26**, 1209 (1964); J. K. Ruff and G. Paulett, *Inorg. Chem.*, **3**, 998 (1964). Also see R. J. Clark and P. I. Hoberman, *Chem. Eng. News*, **42**, No. 43, 52 (1964).

[3] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964).

[4] J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

[5] E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.* **81**, 6363 (1959).

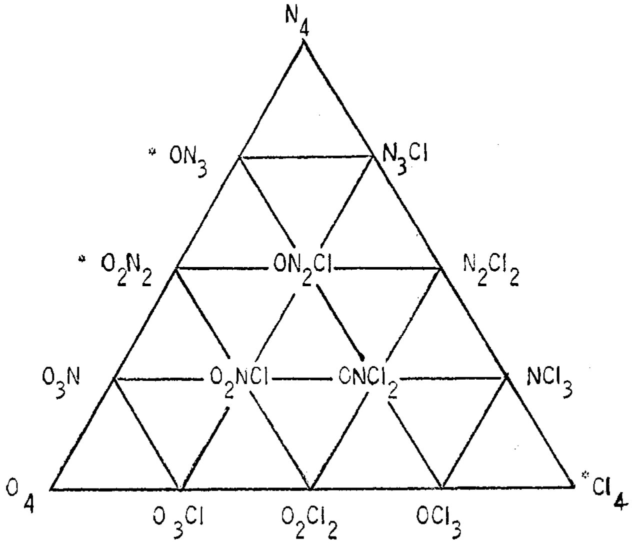

Figure 1.—Schematic diagram showing the 15 possible compounds in the system $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$, where the symbol $O_iN_jCl_{4-i-j}$ stands for the compound $Si(OCH_3)_i[N(CH_3)_2]_jCl_{4-i-j}$, with i and j having independent integer values from 0 to 4 and $i + j \leq 4$. The three compounds marked with an asterisk were not found in detectable amounts in the systems studied in this investigation.

Figure 1. In this investigation, we studied the compositions corresponding to the three completely mixed compounds appearing toward the center of the triangular diagram of this figure plus three sets of six compositions not far from the stoichiometry of each of these three mixed species. The six mixtures of each set lay a short distance out from a given mixed compound on the three lines which cross at each of the mixed compounds in Figure 1. This means that equilibrium measurements were obtained on 21 different compositions. However, the kinetic studies were restricted to the three compositions corresponding to the three completely mixed compounds.

As indicated in Figure 1, three of the 15 possible compounds were not seen in the compositions examined in this study. In the previous investigation[3] dealing with the edges of the triangular diagram of this figure, equilibrium data could not be obtained for the system $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ because the rate of exchange was very slow, being of the same order of magnitude as the rates of side reactions involving breakup of the methoxyl and dimethylamino groups. Since no products from such side reactions were observed in this study, it appears that the presence of the readily exchangeable chlorine accelerates the interchange of methoxyl and dimethylamino groups (perhaps by an indirect kinetic path) so that equilibrium in the $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ system could probably be reached by adding a small amount of silicon tetrachloride as a catalyst.

Equilibrium Studies.—The equilibrium data are presented in Table I, in which the measurements of the individual species are given, along with their experimental errors. No n.m.r. peaks corresponding to compounds other than those listed in Table I were seen. Since all of the experimental data correspond to compositions at or near one of the three compounds containing methoxyl, dimethylamino, and chloro groups, the equilibrium constants which can be obtained from these measurements will necessarily include at least one of these three completely mixed compounds. Of the 39 possible constants involving either two or three other molecules interacting to form a completely mixed molecule, only 12 could be calculated from the data, since three compounds were missing from the total of 15 possible ones. The formulations of these 12 constants are given in Table II along with a listing of the number of individual values determined for each. In addition, the weighted-mean value of each constant is accompanied by two standard errors[6] calculated by computer. The standard error "from data" was calculated by using the errors given in Table I for each of the measured n.m.r. peaks; whereas the other designated "from constants" was obtained from the weighted distribution of the individually determined constants, for each one of which the error "from data" had been calculated and was used as the weighting factor. In these computations, the two sets of values denoted by footnote *c* in Table I were omitted because the equilibrium constants obtained from them were in poor agreement with those based on the 19 other sets of data of Table I. The final column of Table II gives the theoretical random values for the equilibrium constants—values calculated[7] on the basis that the methoxyl, dimethylamino, and chloro groups are not preferentially scrambled.

The 12 equilibrium constants of Table II are interrelated to themselves and to the previously published[3] equilibrium constants. This allows multiple cross checking of the values. In most cases, the results obtained from cross checking agree very closely (well within the standard deviations) with the weighted-average values reported in Table II. However, this was not true of K_1 and K_8, for which we believe the best values are 0.3 and 0.04, respectively. The method of cross checking between constants as well as the calculation of the value of 0.3 instead of 0.18 for K_1 is illustrated by the relationships

$$K_1 = K_9^3K_2^2/K_7^2 = 0.41 \tag{1}$$

$$K_1 = K_8K_2/K_7 = 0.13 \tag{2}$$

$$K_1 = K_4K_9^2K_2/K_7 = 0.37 \tag{3}$$

$$K_1 = K_{11}K_AK_3/K_BK_{12} = 0.27 \tag{4}$$

where K_A and K_B were measured previously[3] with

$$K_A = [Si(OCH_3)_4][Si(OCH_3)_2Cl_2]/[Si(OCH_3)_3Cl)^2 = 0.0089 \tag{5}$$

$$K_B = [Si[N(CH_3)_2]_3Cl][Si[N(CH_3)_2]Cl_3]/[Si[N(CH_3)_2]_2Cl_2]^2 = 6 \times 10^{-4} \tag{6}$$

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(6) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964). Also some similar mathematics not yet published.

(7) Combinatorial analysis shows that for the equilibrated compositions corresponding to over-all mole ratios of the exchangeable substituents Z:T:X equal to either 2:1:1 or 1:1:1 in the system QZ_4 *vs.* QT_4 *vs.* QX_4, the following relative amounts of the various compounds should be observed, assuming statistically random sorting of the Z, T, and X substituents on a tetrafunctional Q atom or moiety. The notation Z_iT_j,X_{4-i-j} stands for the compound $QZ_iT_jX_{4-i-j}$ and the values for Z:T:X = 2:1:1 are presented first, followed by the values in parentheses for Z:T:X = 1:1:1. The relative amounts are Z_2TX, 48 (12); $ZT_2X = ZTX_2$, 24 (12); $Z_3T = Z_3X$, 32 (4); $Z_2T_2 = Z_2X_2$, 24 (6); $ZT_3 = ZX_3$, 8 (4); $T_3X = TX_3$, 4 (4); T_2X_2, 6 (6); Z_4, 16 (1); and $T_4 = X_4$, 1 (1).

TABLE I

DATA AND ERROR AS PERCENTAGE OF TOTAL SILICON IN EQUILIBRATED MIXTURES AT 120°

Over-all Mole Ratios for Si = 1 from mixing		from n.m.r. assuming no $SiCl_4$		O_4[a]	O_3N	N_4	N_3Cl	N_2Cl_2	NCl_3	O_3Cl	O_2Cl_2	O_2NCl	ON_2Cl	$ONCl_2$
O/Cl	N/Cl	O/Cl	N/Cl	O_2NCl Composition Region										
2.07	1.03	2.06	1.07	16.3(0.7)[b]	5.2(0.4)		7.6(0.2)	18.3(0.7)		14.8(0.4)		35.2(1.2)	2.6(1.3)	
1.72	0.79	1.40	0.64	1.8(0.3)	2.4(0.4)		1.2(0.2)	11.4(0.3)		16.8(0.4)	12.6(0.6)	35.9(1.9)		18.0(1.3)
2.47	1.48	2.38	1.44	24.1(0.6)	8.7(0.4)		16.9(0.6)	15.1(0.6)		9.9(0.4)		20.4(0.6)	4.9(1.2)	
2.25	1.08	2.29	1.10	16.7(0.7)	7.1(0.5)	5.9(0.1)		14.7(0.7)		17.8(0.5)		34.0(0.7)	4.0(1.3)	
1.42	0.81	1.53	0.85	3.7(0.6)	4.9(0.4)		11.6(0.4)	13.4(0.6)		20.3(0.4)	6.7(0.6)	31.0(1.2)		8.5(1.2)
1.77	1.03	1.70	0.98	7.4(0.1)	5.4(0.1)	3.8(0.3)	6.9(0.3)	14.8(0.3)		20.7(0.9)	3.4(0.7)	33.7(1.3)	4.0(1.3)	
2.14	0.80	2.16	0.79[c]	8.4(0.3)	5.1(0.4)	0.6(0.6)	3.6(0.2)	5.2(0.8)		21.1(0.4)	4.2(0.6)	44.7(1.2)	2.4(1.2)	4.8(1.2)
				ON_2Cl Composition Region										
0.97	1.93	0.97	1.84	17.6(0.7)	2.9(0.4)		42.1(0.9)	23.8(0.8)		1.9(0.5)		5.9(0.7)	5.9(1.5)	
0.94	1.71	0.94	1.62	5.8(0.4)	3.7(0.5)		34.4(1.0)	17.0(0.7)		6.7(0.5)		10.2(0.7)	7.3(1.5)	
1.45	2.99	1.35	2.81	22.0(0.9)	2.4(0.6)		67.3(1.5)	2.8(0.5)		1.8(0.6)			3.7(1.8)	
1.27	2.40	1.20	2.22	17.3(0.8)	3.9(0.6)		46.9(0.8)	13.1(0.4)		2.8(0.6)		4.2(0.8)	3.4(1.7)	
0.72	1.74	0.73	1.75	8.0(0.4)	3.5(0.6)	1.4(0.3)	38.3(1.2)	28.7(0.9)		5.9(0.7)		8.8(0.9)	5.3(1.8)	
0.93	2.13	0.98	2.06	16.4(0.4)	3.8(0.6)	0.8(0.2)	48.2(1.1)	20.1(0.4)		3.3(0.5)		4.1(0.8)	3.3(1.6)	
1.20	1.91	1.23	2.12	15.5(0.4)	5.2(0.6)	0.6(0.4)	37.3(1.1)	20.2(0.4)		5.7(0.6)		10.3(0.9)	5.2(1.7)	
				$ONCl_2$ Composition Region										
0.49	0.51	0.49	0.52					25.2(0.9)	8.7(0.6)	2.1(0.4)	20.5(0.6)	6.2(0.6)		37.3(1.2)
0.48	0.44	0.49	0.46					16.3(0.6)	13.0(0.6)	1.6(0.4)	20.1(0.6)	4.1(0.6)		44.9(1.2)
0.57	0.71	0.56	0.68					42.4(0.6)	1.8(0.6)	8.0(0.4)	17.9(0.6)	9.6(0.6)	6.0(1.2)	14.3(1.2)
0.57	0.52	0.56	0.53					25.0(0.9)	5.3(0.6)	3.9(0.4)	20.0(0.6)	9.4(0.6)	1.2(1.2)	35.3(1.2)
0.37	0.47	0.37	0.58					23.8(0.6)	18.6(0.6)	0.8(0.4)	18.6(0.6)	2.3(0.6)		31.3(1.2)
0.46	0.56	0.47	0.64					31.0(0.6)[d]	13.2(0.6)	3.1(0.4)	20.1(0.6)	5.2(0.6)	1.2(1.2)	26.4(1.2)
0.62	0.42	0.67	0.40[c]					7.9(0.3)	8.5(0.6)	2.4(0.4)	20.0(0.6)	9.7(0.6)	0.6(0.6)	50.9(1.2)

[a] The symbolism used for the various silicon compounds in Fig. 1 is employed here, where the compound $Si(OCH_3)_i[N(CH_3)_2]_jCl_{4-i-j}$ is represented by $O_iN_jCl_{4-i-j}$.

[b] Error in values as estimated from inspection of the n.m.r. peaks.

[c] Values omitted in calculating the equilibrium constants of Table II because of excessive deviations from the mean.

[d] This is the only experiment in which the OCl_3 compound was observed. Found: 4.6% of the total Si; calculated: 1.2%.

TABLE II

EQUILIBRIUM CONSTANTS FOR SCRAMBLING AT 120° IN THE SYSTEM $Si(OCH_3)_4$ *vs.* $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$

Equilibrium constants[a]	No. of meas.	Av. value[b]	Standard error[b] from data	from constants	Theor. random value[7]
$K_1 = [O_2NCl]^3/[N_3Cl][O_3Cl]^2$	9	0.18	0.06	0.12	27
$K_2 = [O_2NCl]^3/[O_3N][N_2Cl_2][O_3Cl]$	19	0.87	0.12	1.6	18
$K_3 = [O_2NCl]^2/[O_4][N_2Cl_2]$	7	0.18	0.04	0.3	24
$K_4 = [O_2NCl]^2/[ON_2Cl][O_3Cl]$	7	2.4	0.7	0.8	3
$K_5 = [O_2NCl]^2/[O_3N][ONCl_2]$	2	34	6	11	3
$K_6 = [ON_2Cl]^4/[O_4][N_3Cl]^2[N_2Cl_2]$	16	0.002	0.001	0.001	216
$K_7 = [ON_2Cl]^3/[O_3N][N_3Cl][N_2Cl_2]$	16	0.02	0.01	0.03	18
$K_8 = [ON_2Cl]^3/[N_3Cl]^2[O_3Cl]$	8	0.003	0.005	0.005	27
$K_9 = [ON_2Cl]^2/[N_3Cl][O_2NCl]$	10	0.06	0.03	0.04	3
$K_{10} = [ONCl_2]^3/[N_2Cl_2][NCl_3][O_3Cl]$	12	9.8	1.6	13	18
$K_{11} = [ONCl_2]^2/[O_2Cl_2][N_2Cl^2]$	6	1.7	0.15	0.96	4
$K_{12} = [ONCl_2]^2/[O_2NCl][NCl_3]$	5	17	4	12	3

[a] The notation for the constants is the same as that employed in Figure 1, where $Si(OCH_3)_i[N(CH_3)_2]_jCl_{4-i-j}$ is represented by $O_iN_jCl_{4-i-j}$. [b] Calculated[6] from the data of Table I.

The theory of scrambling equilibria demands that each of the three completely mixed compounds based on methoxyl, dimethylamino, and chloro groups be present at maximum concentration at the composition corresponding to its stoichiometry. By our measurements, these maximum equilibrated amounts were 35% of the total Si for $Si(OCH_3)_2[N(CH_3)_2]Cl$, 6% for $Si(OCH_3)[N(CH_3)_2]_2Cl$, and 37% for $Si(OCH_3)[N(CH_3)_2]Cl_2$. Had the system been completely random,[7] these three concentrations would have been identical and equal to 18.8% of the total Si.

Kinetic Runs.—Figure 2 shows the kinetic data obtained on a starting composition in which 1 mole each of $Si(OCH_3)_4$ and $Si[N(CH_3)_2]_4$ were combined with 2 moles of $SiCl_4$. In order to obtain reasonable spacing of the points in plotting this figure, the time axis is presented on a cube-root scale, with no theoretical significance being implied. Both the $SiCl_4$ and the $Si[N(CH_3)_2]_4$ have dropped to essentially zero in the first hour; whereas it takes about 6 hr. for the first detectable amount of reaction of the $Si[N(CH_3)_2]_iCl_{4-i}$ compounds with the slow-acting reagent, $Si(OCH_3)_4$.

Except for the fact that the $SiCl_4$ had completely disappeared before the first experimental point was taken at *ca.* 9 min., rate curves similar to those of Figure 1 were observed when the mole ratios of the starting ingredients $Si(OCH_3)_4$:$Si[N(CH_3)_2]_4$:$SiCl_4$ equaled either 2:1:1 or 1:2:1 instead of the 1:1:2 of Figure 2. In all three cases, the compound $Si[N(CH_3)_2]Cl_3$ was found to maximize within the first 0.5 hr.; however, for the 1:2:1 ratio of starting ingredients, the compound $Si[N(CH_3)_2]_2Cl$ did not maximize. On the assumption that the scrambling reactions occur through interchange of two unlike substituents between a pair of

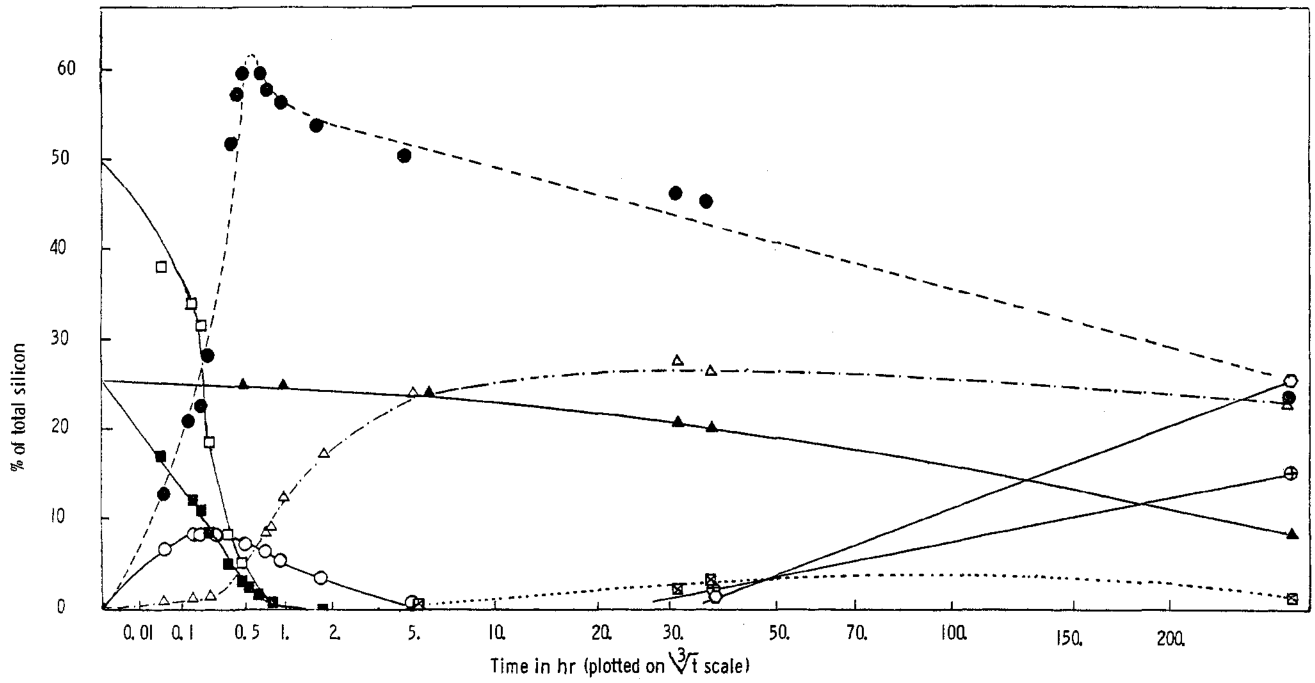

Figure 2.—Variation with time at 38.5° of the various compounds formed upon mixing 2 moles of $SiCl_4$ with 1 mole each of $Si(OCH_3)_4$ and $Si[N(CH_3)_2]_4$. The symbolism describing the various compounds is the same as that employed in Figure 1: ■, N_4; ○, N_3Cl; △, N_2Cl_2; ●, NCl_3; □, Cl_4; ▲, O_4; ⊠, O_3Cl; ⊕, O_2Cl_2; ⟨‾⟩, $ONCl_2$.

molecules, we see that the very first reaction must be the following, where the notation $O_iN_jCl_{4-i-j}$ stands for $Si(OCH_3)_i[N(CH_3)_2]_jCl_{4-i-j}$

$$N_4 + Cl_4 \longrightarrow NCl_3 + N_3Cl \quad (7)$$

The next two reactions must be considerably faster than that of eq. 7. They are

$$N_3Cl + Cl_4 \longrightarrow N_2Cl_2 + NCl_3 \quad (8)$$

$$N_2Cl_2 + Cl_4 \longrightarrow 2NCl_3 \quad (9)$$

On the other hand, the curves indicate that the reaction of eq. 10 is slower than that of eq. 7.

$$NCl_3 + N_3Cl \longrightarrow 2N_2Cl_2 \quad (10)$$

An even slower reaction for the ratios of O_4:N_4:Cl_4 of either 2:1:1 or 1:2:1 is

$$N_4 + NCl_3 \longrightarrow N_3Cl + N_2Cl_2 \quad (11)$$

We now come to the reactions with tetramethyl silicate, which are extremely slow compared to the preceding ones. In the case of the data given in Figure 2, the first of these reactions appear to be

$$O_4 + NCl_3 \longrightarrow ONCl_2 + O_3Cl \quad (12$$

$$NCl_3 + O_3Cl \longrightarrow ONCl_2 + O_2Cl_2 \quad (13)$$

Succeeding scrambling reactions also involve exchange of methoxyl groups with chlorine atoms, such as

$$O_2Cl_2 + NCl_3 \longrightarrow ONCl_2 + OCl_3 \quad (14)$$

$$OCl_3 + O_3Cl \longrightarrow 2O_2Cl_2 \quad (15)$$

Assuming that reactions 7 through 15 are bimolecular, the rate constant of reaction 7 is estimated to be *ca.* 2×10^{-3} l./mole sec., with reactions 8 and 9 being approximately 10 and 30 times faster. On this same basis, the rate constants of reactions 10 and 11 are *ca.* 2×10^{-5} and *ca.* 1×10^{-4} l./mole sec., respectively. The reaction of eq. 12 is about a thousandfold slower than that of eq. 7 (*i.e.*, for reaction 12, $k \approx 10^{-6}$ l./mole sec.). The reader is referred to Figures 5 through 7 of ref. 3 for similar data which can be explained by the reaction scheme of eq. 7 through 11, using approximately the same rate constants as the estimated values given here.