calculations are summarized in Table IV. The total number of geometrical isomers of $Nb_2Cl_2(C_2H_5O)_6(C_5H_5N)_2$, with the restrictions that (1) each niobium is surrounded octahedrally by ligands, (2) each niobium is bonded to only one pyridine molecule, and (3) pyridine molecules cannot act as bridging ligands, is 70.

Calculation of the total number of geometrical isomers by considering the eight distinguishable ways to distribute two pyridines on the eight nonbridging positions[13] separately yields 123. This agrees with our preceding result.

[13] The number eight was calculated from the cycle index for the D_{2h} point group.

CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
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Scrambling of Methoxyl, Dimethylamino, and Chloro Groups on Silicon[1]

BY KURT MOEDRITZER[2] AND JOHN R. VAN WAZER

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By means of gas chromatography, quantitative data were obtained on ester interchange between tetramethyl and tetraethyl silicates (1) $Si(OCH_3)_4$ *vs.* $Si(OC_2H_5)_4$. H^1 nuclear magnetic resonance was used to investigate the systems: (**2**) $Si(OCH_3)_4$ *vs.* $SiCl_4$ and (**3**) $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$. The equilibria for the esters (system 1) are close to those expected for ideal random interchange. However, the mixed species are greatly favored in the exchanges involving silicon tetrachloride. The deviation from ideal random behavior is larger in the case of exchange of dimethylamino groups with chlorines than in the case of alkoxyl groups with chlorines. This is similar to the situation found with the analogous phosphorus compounds. Measurements are presented on the rates of exchange of chlorine for either methoxyl or dimethylamino groups.

Although there is a considerable body of literature[3] on the redistribution reactions of alkoxyl groups, halogens, and amino groups on silicon, it is very difficult to determine from this literature whether or not equilibrium was reached. In studies of redistribution reactions, it is important to obtain the equilibrium values, since large deviations from the equilibria corresponding to random sorting may be the cause of unusually high or low yields in preparative chemistry. Such deviations are also important to the understanding of the chemistry of these compounds, as explained in the Discussion section of this paper.

Unlike the previous authors, we took special care in this study to separate rate phenomena from the equilibria. As a result, it is now possible to determine whether the data reported in the previous literature correspond to partial or complete equilibration. By treating the equilibria in terms of deviations of the corresponding free energies from those expected for completely random exchange, we have been able to compare on a logical basis the results obtained on compounds of silicon with those found for analogous compounds of phosphorus.

Experimental

Tetramethyl silicate, tetraethyl silicate, and silicon tetrachloride were repurified by careful distillation in a dry atmosphere from commercial samples obtained from the Anderson Chemical Company. The tetrakis(dimethylamino)silane (*i.e.*, octamethylsilanetetramine) was prepared[4] from silicon tetrachloride and was also carefully purified by fractionation. In all cases, middle cuts having a constant boiling point were taken from a fractionating column with *ca.* 20 theoretical plates.

Ester Interchange.—The substituent-exchange reaction between tetramethyl silicate and tetraethyl silicate was carried out in sealed glass tubes at 150°. Analyses were performed by gas chromatography using a Perkin-Elmer vapor fractometer, Model 154D, with a printing integrator. A 2-m. column containing C-22 firebrick supporting 10% of Tween 80 was employed at a temperature of 80°. The retention times of tetramethyl silicate and tetraethyl silicate were identified through runs on the pure samples, and assignment of the chromatographic peaks due to the mixed esters was made from their sequence and checked by material-balance calculations. The retention times were found to increase more than linearly with substitution of ethyl for methyl.

Redistribution between the tetramethyl and tetraethyl silicates was found to reach equilibrium within *ca.* 4 days at 150°. The data reported here correspond to 10 days at that temperature.

Exchanges with $SiCl_4$.—Equilibrium measurements for the reactions between silicon tetrachloride and either tetramethyl silicate or tetrakis(dimethylamino)silane were made at room temperature on samples heated in sealed glass tubes at 120° for 200 hr. in the case of the first system and 18 hr. for the second. These heating times were chosen on the basis of rate studies. However, because of fast re-equilibration at room temperature (see Fig. 5–7) the equilibrium data on the system $Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$ correspond to a temperature between 25 and 37°, since the samples stood overnight at room temperature and the n.m.r. measuring probe operates at 37°. Contrary to the data of Kumada,[3] samples with low $SiCl_4$ content took somewhat longer

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[1] Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 22, 1962.

[2] On leave of absence from the Inorganic Chemicals Division of Monsanto, July, 1961–1962.

[3] D. F. Peppard, W. G. Brown, and W. C. Johnson, *J. Am. Chem. Soc.*, **68**, 73 (1946); M. Kumada, *J. Inst. Polytech. Osaka City Univ. Ser. C*, **2**, 139 (1952) [*Chem. Abstr.*, **48**, 11303g (1954)]; Yu N. Vol'nov, *J. Gen. Chem. USSR*, **17**, 1428 (1947); K. Schaarschmidt, *Z. anorg. allgem. Chem.*, **310**, 69 (1961). Also, for example, F. C. Boye and H. W. Post, *J. Org. Chem.*, **17**, 1389 (1952), and K. A. Andrianov, S. A. Golubtsov, and N. P. Lobusevich, *Zh. Obsch. Khim.*, **26**, (1956); *J. Gen. Chem. USSR*, **26**, 207 (1956). For reviews of the chemistry studied here, see C. Eaborn, "Organosilicon Compounds," Butterworth, London, 1960, and R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

[4] H. Breederveld and H. I. Waterman, *Research* (London), **5**, 537 (1952).

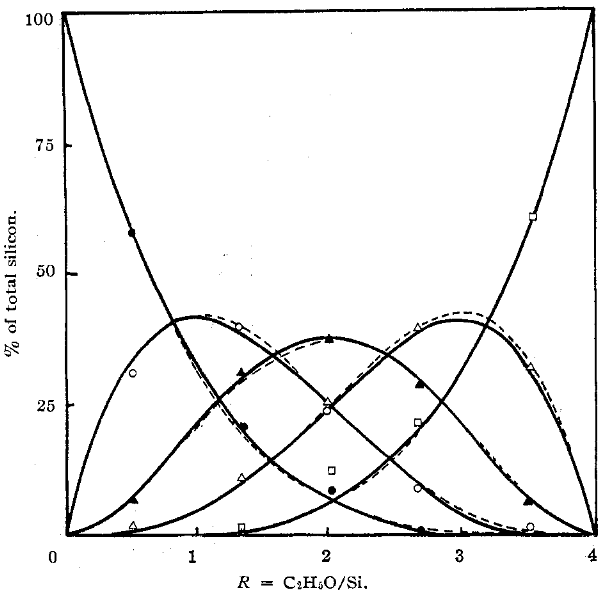

Fig. 1.—Equilibration at 150° between tetramethyl silicate and tetraethyl silicate. The solid lines correspond to $K_1 = 0.417$, $K_2 = 0.422$, and $K_3 = 0.386$, and the dashed lines to random substituent interchange: ●, $Si(OCH_3)_4$; ○, $Si(OCH_3)_3(OC_2H_5)$; ▲, $Si(OCH_3)_2(OC_2H_5)_2$; △, $Si(OCH_3)(OC_2H_5)_3$; □, $Si(OC_2H_5)_4$.

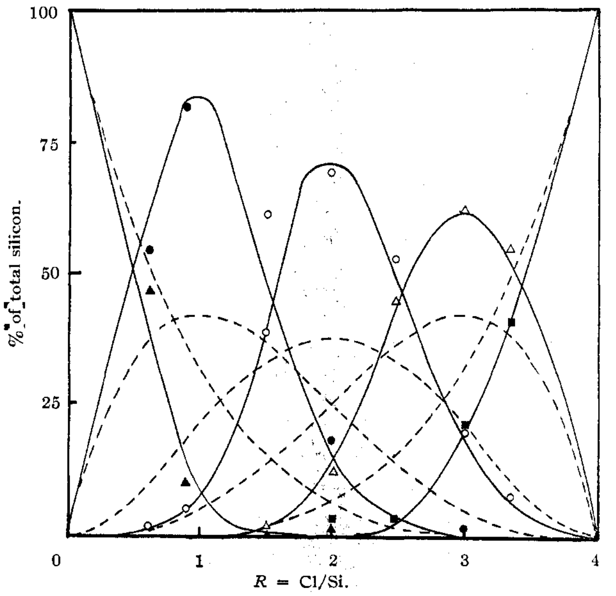

Fig. 2.—Equilibration at 120° between tetramethyl silicate and silicon tetrachloride. The dotted lines correspond to random substituent interchange and the solid lines to $K_1 = 0.094$, $K_2 = 0.042$, and $K_3 = 0.0089$: ▲, $Si(OCH_3)_4$; ●, $ClSi(OCH_3)_3$; ○, $Cl_2Si(OCH_3)_2$; △, $Cl_3Si(OCH_3)$; ■, $SiCl_4$.

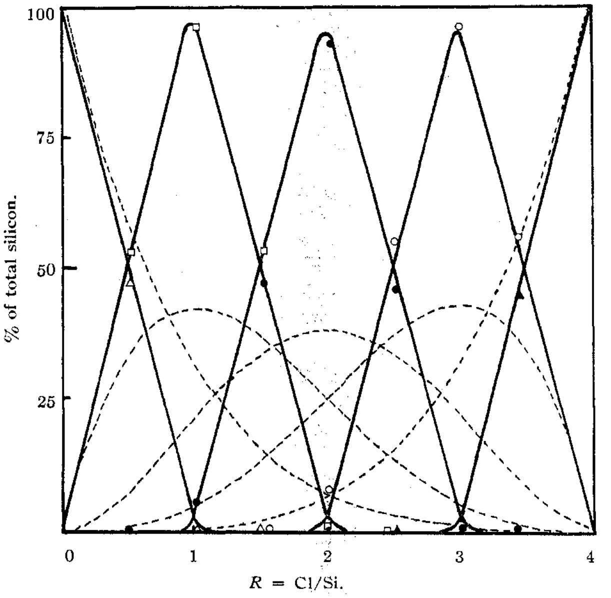

Fig. 3.—Equilibration at 25° between tetrakis(dimethylamino)-silane and silicon tetrachloride. The dotted lines correspond to random substituent interchange and the solid lines to $K_1 = K_2 = 6 \times 10^{-4}$ and $K_3 = 6 \times 10^{-6}$: △, $Si[N(CH_3)_2]_4$; □, $ClSi[N(CH_3)_2]_3$; ●, $Cl_2Si[N(CH_3)_2]_2$; ○, $Cl_3Si[N(CH_3)_2]$; ▲, $SiCl_4$.

to equilibrate in the $Si(OCH_3)_4$–$SiCl_4$ system. When silicon tetrachloride was combined with tetrakis(dimethylamino)silane, considerable heat was given off but the reaction was too slow for quantitative determinations of the heat of reaction with the simple dewar-flask calorimeter used in our laboratory.

H^1 nuclear magnetic resonance (n.m.r.) was employed for analysis of these two systems. In the case of the system involving tetramethyl silicate, the proton spectrum of the O-methyl groups was employed, and, for the system involving tetrakis(dimethylamino)silane, the proton spectrum of the N-methyl groups was used. For both systems, silicon tetrachloride was determined by difference. A Varian A-60 analytical spectrometer running at a frequency of 60 Mc. was employed for the n.m.r. determinations, using a sweep rate of 0.1 c.p.s. at the most expanded sweep width (50 cycles for the entire scale). The n.m.r. chemical shifts as measured from tetramethylsilane dissolved in the samples (not extrapolated to infinite dilution) are reported in terms of τ values[5] as follows: $Si(OCH_3)_4$, 6.48; $ClSi(OCH_3)_3$, 6.45; $Cl_2Si(OCH_3)_2$, 6.37; $Cl_3Si(OCH_3)$, 6.28; $Si[N(CH_3)_2]_4$, 7.56; $Si[N(CH_3)_2]_3Cl$, 7.50; $Si[N(CH_3)_2]_2Cl_2$, 7.42; and $Si[N(CH_3)_2]Cl_3$, 7.31 p.p.m.

Results and Conclusions

Reorganization Equilibria.—The experimental data are presented in Fig. 1–3, from which it can be seen that the ester interchange is essentially random, whereas the exchange of methoxyl groups with chlorine is considerably less random, with extreme nonrandom behavior being found in exchange of dimethylamino groups with chlorine. The equilibrium constants calculated from the data of Fig. 1–3 are given in Table I. These equilibrium constants are of the forms

$$K_i = [SiZ_{i+1}T_{3-i}][SiZ_{i-1}T_{5-i}]/[SiZ_iT_{4-i}]^2 \qquad (1)$$

where T = Cl or C_2H_5O, Z = OCH_3 or $N(CH_3)_2$ and i may have the values of 1, 2, or 3. Also note that $R = [T]/[Si]$.

Statistical study of the data, as outlined in a previous paper from this laboratory,[6] indicates that variation in activity coefficients is sufficiently large so as to be barely discernible for only two of the nine equilibrium constants—those for which $Si(OCH_3)(OC_2H_5)_3$ and $Si(OCH_3)Cl_3$ are in the denominator of eq. 1.

The majority of previous investigators[3] presented data which were far from equilibrium. However, our data show that the measurements of Peppard, Brown, and Johnson and those of Kumada were either

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[5] $\tau = 10 + \delta$, where δ is the chemical shift in p.p.m. as measured from tetramethylsilane, and a positive value of δ corresponds to an upfield shift.

[6] L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, accepted for publication.

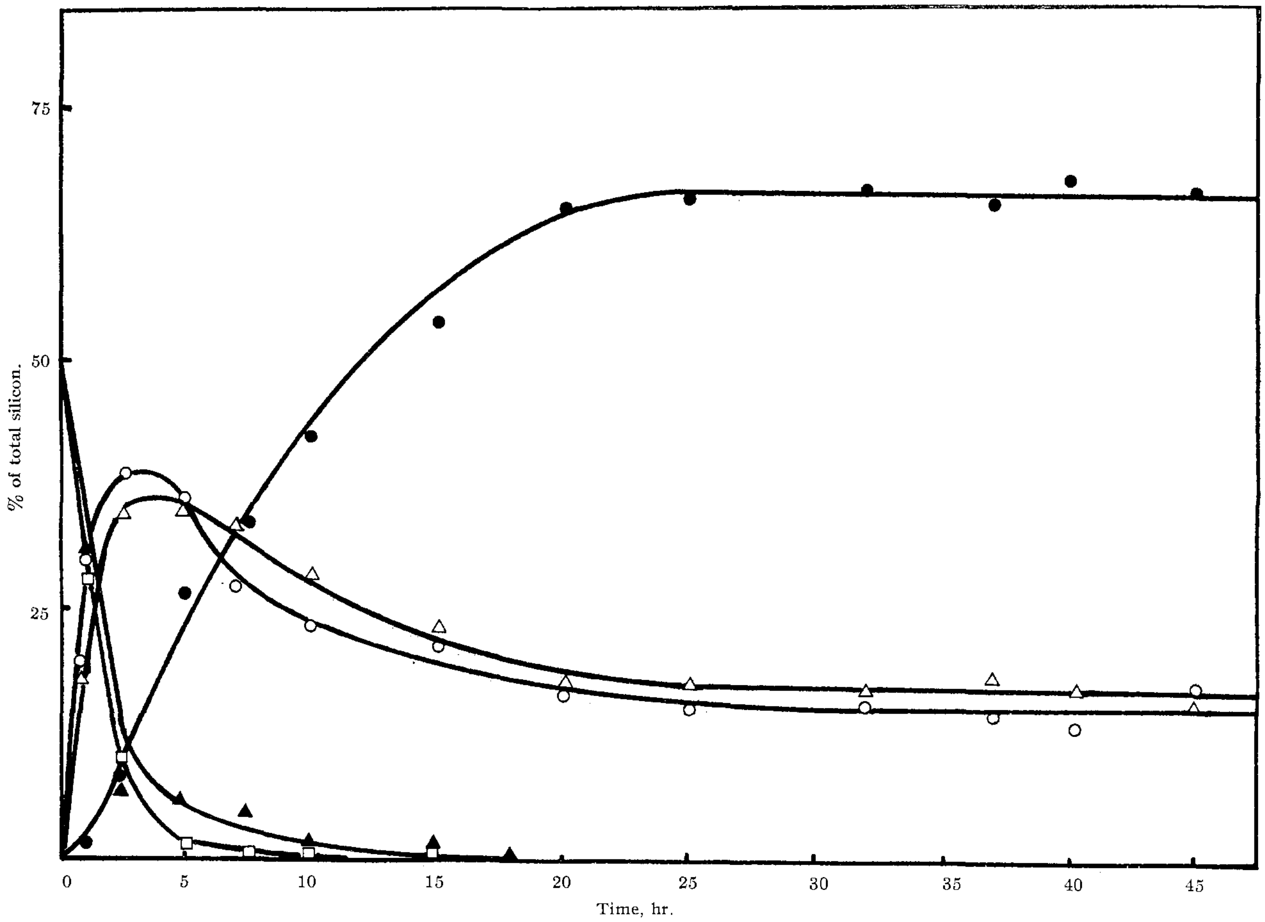

Fig. 4.—Rate of equilibration of a mixture of 1 mole of tetramethyl silicate with 1 mole of silicon tetrachloride at 120°: □, $Si(OCH_3)_4$; △, $ClSi(OCH_3)_3$; ●, $Cl_2Si(OCH_3)_2$; ○, $Cl_3Si(OCH_3)$; ▲, $SiCl_4$.

TABLE I

EQUILIBRIUM CONSTANTS FOR LIGAND INTERCHANGE BETWEEN SOME SILICON MOLECULES

$Si(OCH_3)_4$ *vs.* $Si(OC_2H_5)_4$ error[a] = 0.98% of total Si
$K_1 = 0.417$, $s = 0.026$[b]
$K_2 = 0.422$, $s = 0.025$
$K_3 = 0.386$, $s = 0.025$

$Si(OCH_3)_4$ *vs.* $SiCl_4$ error[a] = 2.3% of total Si
$K_1 = 0.094$, $s = 0.019$[b]
$K_2 = 0.042$, $s = 0.006$
$K_3 = 0.0089$, $s = 0.003$

$Si[N(CH_3)_2]_4$ *vs.* $SiCl_4$ error[a] = 0.59% of total Si
$K_1 = 6 \times 10^{-4}$, $s = 2 \times 10^{-4}$ or 2×10^{-5}[c]
$K_2 = 6 \times 10^{-4}$, $s = 6 \times 10^{-4}$ or 1×10^{-5}
$K_3 = 6 \times 10^{-6}$, $s = 3 \times 10^{-4}$ or 2×10^{-7}

[a] Standard error of experimental points. [b] Standard error, *s*, of the equilibrium constants from the experimental points. [c] The first value represents the standard error from the experimental points, the second corresponds to the standard error from the weighted values of the individually calculated equilibrium constants. The two values are reported here since they differ greatly for this system.

at or very close to equilibrium. The work of Peppard, *et al.*, plus ours shows that exchange of the shorter-chain *n*-alkoxyl groups on silicon is close to ideal randomness.

Kinetic Results.—A preliminary study was done on the kinetics of the redistribution reactions occurring when equimolar amounts of tetramethyl silicate and silicon tetrachloride were combined at 120°. In this run, there were undoubtedly trace amounts of HCl formed inadvertently in handling the silicon tetrachloride and this may have exhibited catalytic activity. As shown in Fig. 4, the amounts of $Si(OCH_3)_3Cl$ and $Si(OCH_3)Cl_3$ go through maxima, which correspond to approximately twice the equilibrium amounts of these species. It should be noted from this figure that equilibrium is reached in about 25 hr.

Figures 5–7 present kinetic measurements for the equilibration of 3 : 1, 1 : 1, and 1 : 3 molar mixtures of silicon tetrachloride with tetrakis(dimethylamino)-silane at 38° (the temperature of samples held in the probe of the Varian A-60 n.m.r. spectrometer). According to these data, the rate of equilibration of the $Si[N(CH_3)_2]_4$–$SiCl_4$ system would be the order of magnitude of 100-fold faster than that of the $Si(OCH_3)_4$–$SiCl_4$ system at the same temperature. Such a large difference in rate cannot be attributed to a presumed catalyst since the same extent of purification was used for each system—middle cuts of freshly distilled reagents were combined in a dry atmosphere—and the same care was taken to avoid hydrolysis of the silicon tetrachloride by moisture in the air. Although trace amounts of HCl may have been exerting catalytic action in our studies of both systems, it is quite certain that this does not account for the big difference in rate since replicate kinetic runs using either carefully re-

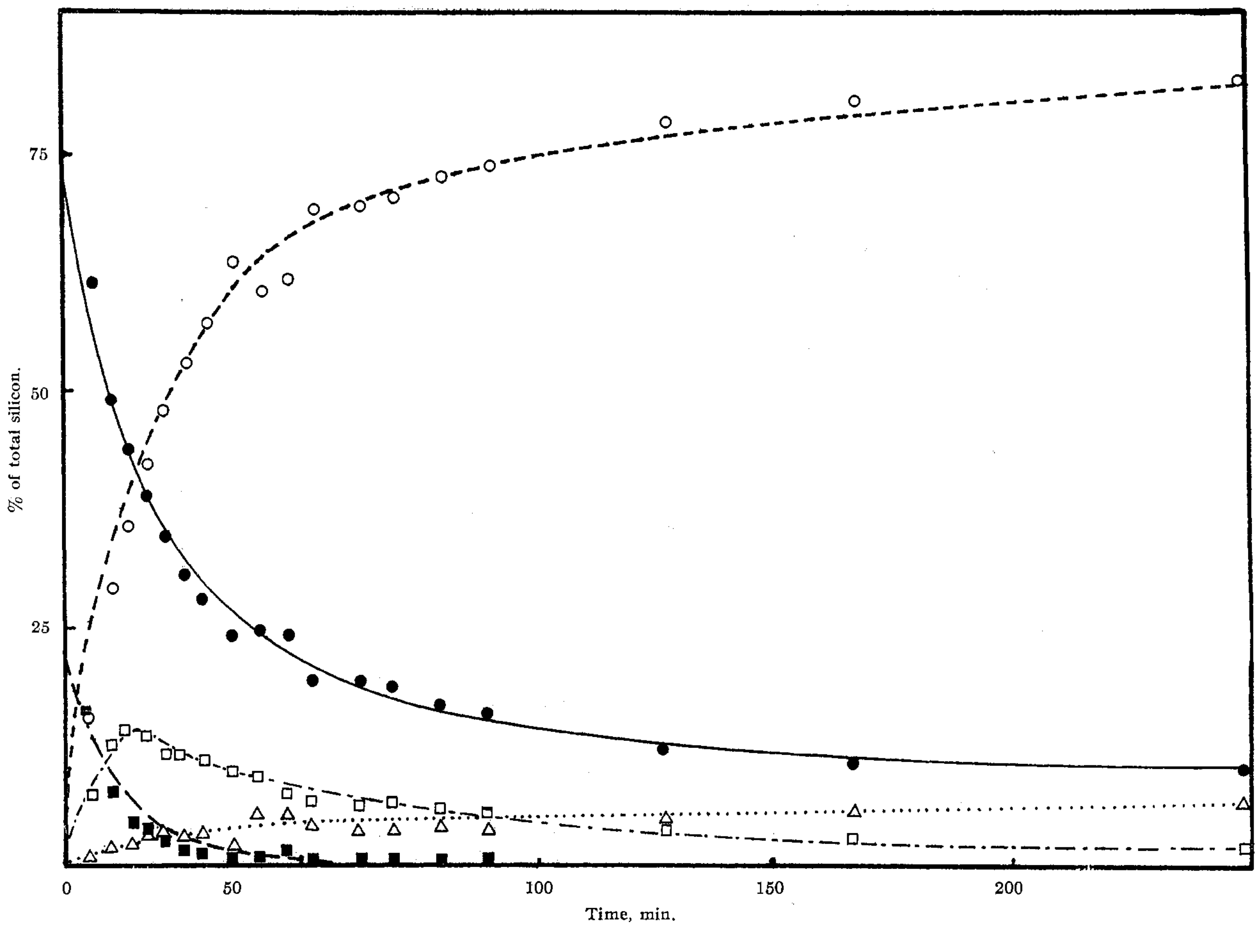

Fig. 5.—Rate of equilibration of 1 mole of tetrakis(dimethylamino)silane with 3 moles of silicon tetrachloride at 38°: ■, $Si[N(CH_3)_2]_4$; □, $ClSi[N(CH_3)_2]_3$; △, $Cl_2Si[N(CH_3)_2]_2$; ○, $Cl_3Si[N(CH_3)_2]$; ●, $SiCl_4$.

distilled or commercially available silicon tetrachloride differed by less than a factor of two.

As the value of R = Cl/Si increases, the rate of equilibration in the system $Si[N(CH_3)_2]_4$–$SiCl_4$ becomes faster. Thus, the experimental half-life for the formation of $SiCl[N(CH_3)_2]_3$ in the composition for which $R = 1.00$ is 4×10^2 min.; for formation of $SiCl_2[N(CH_3)_2]_2$ at $R = 2.00$ it is 2.5×10^2 min.; and, for formation of $SiCl_3[N(CH_3)_2]$ at $R = 3.00$ it is only 20 min.

The mixed compounds, $Si[N(CH_3)_2]_3Cl$ and $Si[N(CH_3)_2]Cl_3$, are seen to go through maxima in Fig. 5–7. The explanation for these maxima as well as for the ones seen in Fig. 4 is as follows: Upon mixing the compound SiZ_4 with the compound SiT_4 (where Z and T stand for two different substituents), the first interchange must give the two products SiZ_3T and $SiZT_3$. As the concentration of these two products increases, the probability of their exchanging substituents with the starting compounds becomes appreciable so that some SiZ_2T_2 is formed. At equilibrium, there will be various amounts of the five compounds having the formula SiZ_iT_{4-i}, where i = 0, 1, 2, 3, or 4. Nontrivial interchange (*i.e.*, new chemical species are formed) of one Z for one T can be achieved in twelve ways from the various pairs of these five compounds. At the start of the reaction, the only available one of these twelve ways is the exchange of a Z from SiZ_4 for a T of SiT_4; but, as the amounts of species other than these two build up, more and more of the twelve ways of exchange come into play until all of them are active. It is apparent from this qualitative discussion that, depending on the relative ease of exchange by these twelve ways, the amounts of the first two compounds being formed (*i.e.*, SiZ_3T and $SiZT_3$) may build up to relatively large values before the proper ways of exchange to diminish their concentrations to the equilibrium values become prominent. A detailed phenomenological theory of ligand-interchange kinetics —assuming second-order reactions for the allowed ways of interchanging—will be presented in a general form for n substituent sites in a subsequent paper.

Discussion

It is interesting to compare the equilibria reported here for silicon compounds with the equilibria previously observed[6–8] for similar phosphorus compounds. A good way for making such a comparison is to discuss the data in terms of the reaction shown in general form by eq. 2, using a ratio of the observed free energy of this reaction to that calculated on the basis of random

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(7) E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961).

(8) J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, in press.

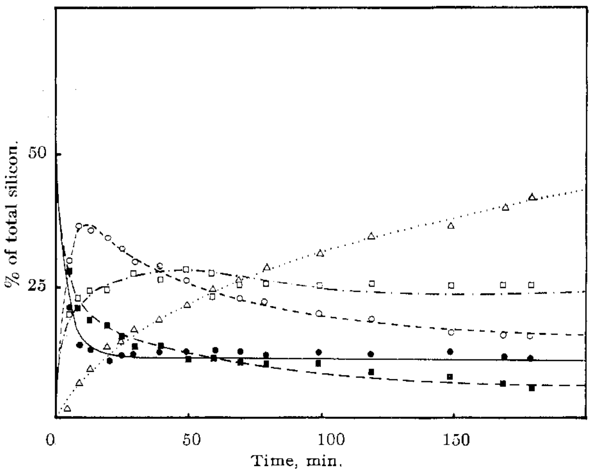

Fig. 6.—Rate of equilibration of 1 mole of tetrakis(dimethylamino)silane with 1 mole of silicon tetrachloride at 38°: ■, $Si[N(CH_3)_2]_4$; □, $ClSi[N(CH_3)_2]_3$; △, $Cl_2Si[N(CH_3)_2]_2$; ○, $Cl_3Si[N(CH_3)_2]$; ●, $SiCl_4$.

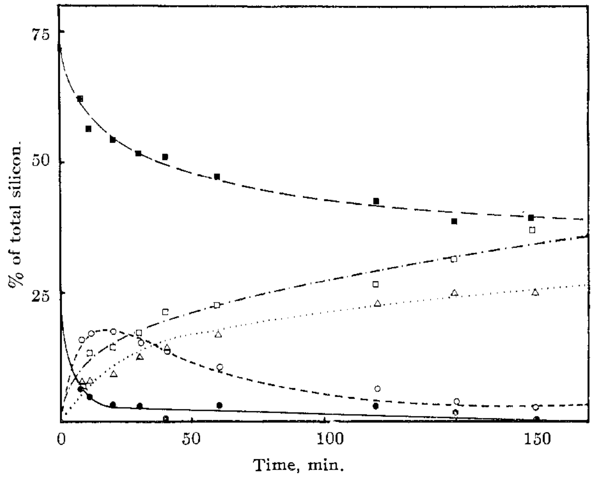

Fig. 7.—Rate of equilibration of 3 moles of tetrakis(dimethylamino)silane with 1 mole of silicon tetrachloride at 38°: ■, $Si[N(CH_3)_2]_4$; □, $ClSi[N(CH_3)_2]_3$; △, $Cl_2Si[N(CH_3)_2]_2$; ○, $Cl_3Si[N(CH_3)_2]$; ●, $SiCl_4$.

sorting of the T and Z substituents so that random interchange is the standard of comparison. Obviously, for Q = Si, n in eq. 2 is 4 and for Q = P, n = 3.

$$(n - i)/n\mathrm{QT}_n + (i/n)\mathrm{QZ}_n = \mathrm{QZ}_i\mathrm{T}_{n-i} \qquad (2)$$

The free-energy deviation from random interchange is presented in eq. 3, where K_{fi} refers to the equilibrium constant of eq. 2.

$$\Delta F_{\mathrm{dev}} = (-RT/n) \ln [K_{fi}/(K_{fi})_{\mathrm{random}}] \qquad (3)$$

where $(K_{fi})_{\mathrm{random}}$ is readily calculated from the binomial coefficients.[9]

The free-energy deviations obtained by use of eq. 3 are nearly completely attributable to nonzero values of the enthalpy and hence may be equated to ΔH for the formation of the mixed species from the end members. Values of $\Delta H \approx \Delta F_{\mathrm{dev}}$ are presented in Table II for the silicon compounds studied here and for similar compounds based on triply-connected phosphorus. As expected, the deviations from ideality are very small for ester interchange and are much larger for interchange of either methoxyl or dimethylamino groups with chlorine atoms. The free-energy deviations from ideality observed for both the silicon and phosphorus compounds roughly parallel the difference in Hammett σ_m constants[10] between chlorine and either the methoxyl or dimethylamino group. Thus, for *meta* substitution on benzene rings, $\Delta\sigma_m$ for $(CH_3)_2N-$ *vs.* Cl– is 0.58 and for CH_3O- *vs.* Cl– it is 0.26.

The most striking feature of Table II is that the deviations from ideality are primarily a function of the substituents and not of the central atom. Work is presently underway in our laboratory to test further this generality, which demonstrates the advantages of using the random state as a basis for comparison. The somewhat greater deviations from ideality seen for the triply-connected phosphorus compounds as compared to the silicon might be attributable in great part to the ease with which triply-connected phosphorus may be rehybridized by incorporating more or less of the s pair of unshared electrons with the three pairs of the bonding p-electrons to give an sp^3 hybrid.[11] According to this explanation, we should expect that the values of ΔF_{dev} would be smaller and more regular for the phosphoryl analogs of the compounds listed in Table II.

TABLE II

FREE-ENERGY DEVIATIONS FROM IDEALLY RANDOM FORMATION

Silicon compound	ΔF_{dev}, kcal./mole	Phosphorus compound	ΔF_{dev}, kcal./mole
$Si(OCH_3)_3(OC_2H_5)$	+0.017	$P(OCH_3)_2(OC_2H_5)$[a]	+0.119
$Si(OCH_3)_2(OC_2H_5)_2$	+0.010	$P(OCH_3)(OC_2H_5)_2$	+0.107
$Si(OCH_3)(OC_2H_5)_3$	+0.052		
$Si(OCH_3)_3Cl$	−3.82	$P(OC_2H_5)_2Cl$[b]	−3.2
$Si(OCH_3)_2Cl_2$	−4.72	$P(OC_2H_5)Cl_2$	−3.2
$Si(OCH_3)Cl_3$	−3.79		
$Si[N(CH_3)_2]_3Cl$	−7.8	$P[N(C_2H_5)_2]_2Cl$[c]	−8.6
$Si[N(CH_3)_2]_2Cl_2$	−9.1	$P[N(C_2H_5)_2]Cl_2$	−9.0
$Si[N(CH_3)_2]Cl_3$	−6.5		

[a] Data from ref. 6. [b] Data from ref. 7. [c] Data from ref. 8

In both the silicon and phosphorus cases, the rates of exchange are found to increase with the free energy of the exchange reaction. This is in agreement with the correlation of reaction rates which has been emphasized most recently by Hammond,[12] who states that "the most stable products are formed at the most rapid rates from a series of similarly constituted reactants."

Acknowledgment.—We wish to thank Messrs. Bruce E. Boggs and Richard A. Kuehne for the gas chromatography measurements.

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(9) G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, **61**, 2748 (1939).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

(11) C. A. Coulson, "Valence," 2nd Ed., Oxford, 1961, p. 221.

(12) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955). This correlation was first proposed by Polanyi, see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.