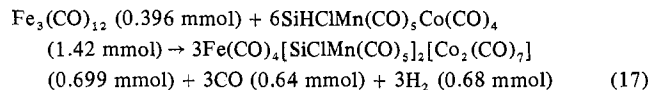


2140 (m), 2115 (s), 2035 (sh), 2000–1980 (s), 1845 (m), 1160–1070 (m), 660 (sh), 650 (m), 635 (w), 540 (m), 500–470 (m), 420 (w), and 340 cm^{-1} (w).

The mass spectrum of the solid was recorded at an ionizing voltage of 80 eV and an instrument temperature of 105°. The inlet was kept at 60°. Prominent ion peaks in the mass spectrum are shown in Table I. No parent peak was observed in this case. Again, the compound apparently decomposes before reaching temperatures at which it is volatile. The amount of $\text{Fe}(\text{CO})_4[\text{SiClMn}(\text{CO})_5]_2[\text{Co}_2(\text{CO})_7]$ obtained was 0.698 g (0.699 mmol). This corresponds to 98.45% yield of $\text{Fe}(\text{CO})_4[\text{SiClMn}(\text{CO})_5]_2[\text{Co}_2(\text{CO})_7]$ based on the amount of $\text{SiHClMn}(\text{CO})_5\text{Co}(\text{CO})_4$ consumed in the reaction shown in eq 17.



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Registry No. SiH_2Cl_2 , 4109-96-0; $\text{NaCo}(\text{CO})_4$, 14878-28-5; $\text{SiH}_2\text{ClCo}(\text{CO})_4$, 41913-72-8; $\text{SiH}_2[\text{Co}(\text{CO})_4]_2$, 23591-62-0; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{SiHCl}_2\text{Co}(\text{CO})_4$, 41913-73-9; $\text{SiCl}_2\text{Co}_2(\text{CO})_7$, 41913-74-0; SiHCl_3 , 10025-78-2; $(\text{CH}_3)_2\text{SiHCl}$, 1066-35-9; $(\text{CH}_3)_2\text{SiHCo}(\text{CO})_4$, 41913-75-1; $\text{NaMn}(\text{CO})_5$, 13859-41-1; $\text{SiH}_2\text{ClMn}(\text{CO})_5$, 20347-37-9; $\text{SiH}_2[\text{Mn}(\text{CO})_5]_2$, 4193-68-2; $\text{SiHClMn}(\text{CO})_5\text{Co}(\text{CO})_4$, 41913-77-3; $\text{SiClMn}(\text{CO})_5\text{Co}_2(\text{CO})_7$, 41913-78-4; $\text{HMn}(\text{CO})_5$, 16972-33-1; $\text{SiCl}_2[\text{Mn}(\text{CO})_5]_2$, 41913-79-5; C_7H_8 , 121-46-0; $(\text{C}_7\text{H}_8)_2$, 16422-76-7; $\text{Fe}_3(\text{CO})_{12}$, 18497-45-5; $\text{Fe}(\text{CO})_4[\text{SiClMn}(\text{CO})_5]_2[\text{Co}_2(\text{CO})_7]$, 41948-82-7.

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Scrambling of Substituents between Dimethylsilicon and Various Methylphosphorus Moieties

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Equilibrium constants have been measured for the scrambling of pairs of substituents between the $(\text{CH}_3)_2\text{Si}<$ and either the $\text{CH}_3\text{P}<$, $\text{CH}_3\text{P}(\text{O})<$, or $\text{CH}_3\text{P}(\text{S})<$ moiety. It is found that, for exchange of chlorine with bromine, the chlorine preferentially bonded to the silicon no matter which phosphorus-containing group is involved. For exchange of chlorine with either a phenoxy or dimethylamino group, the chlorine is preferentially bonded to the silicon in the case of the $\text{CH}_3\text{P}(\text{O})<$ and $\text{CH}_3\text{P}(\text{S})<$ moieties; but the reverse situation is found for the $\text{CH}_3\text{P}<$ moiety. The quantitative equilibrium data are discussed, as are the kinetics of exchange of chlorine and bromine between the dimethylsilicon and the methylthiophosphonyl moieties.

Introduction

Studies of competition equilibria have shown that pairs of exchangeable monofunctional substituents when scrambled between two kinds of polyfunctional central moieties at equilibrium display a pronounced preference of attachment for one kind of central moiety. This has been exemplified earlier for pairs of central moieties based on silicon and germanium¹⁻⁴ and for pairs of variously methyl-substituted silicon moieties⁵⁻⁸ or germanium moieties.⁹ Also reported were scrambling equilibria between methylgermanium and various methylphosphorus moieties.^{10,11} The present paper reports additional studies of this general type, with the exchange of substituents being between dimethylsilicon and

various methylphosphorus groups: $\text{CH}_3\text{P}<$, $\text{CH}_3\text{P}(\text{O})<$, and $\text{CH}_3\text{P}(\text{S})<$.

Experimental Section

Reagents. Dimethyldichlorosilane and dimethyldimethoxysilane were obtained from the Anderson Chemical Co., Weston, Mich., and were fractionated before use. Dimethyldibromosilane,¹² dimethylbis(methylthio)silane,¹³ and dimethylbis(dimethylamino)silane¹⁴ were made according to the literature. Dimethyldiphenoxysilane, bp 95° (0.8 mm), was prepared from dimethyldichlorosilane, phenol, and triethylamine in petroleum ether as solvent. Diphenyl methylphosphonate was obtained in a similar manner, bp 130–133° (0.5 mm). Methylchlorophosphine,¹⁵ methylphosphonic dichloride,¹⁶ and methylphosphonothioic dichloride¹⁷ were prepared according to the literature.

Procedures. Sample preparation, equilibration, proton nuclear magnetic resonance (nmr) measurements, and the calculation of weighted-average equilibrium constants were performed as previously reported.^{1,3} The proton nmr chemical shifts of the methyl groups directly attached to both the silicon and the phosphorus atoms as well as of SCH_3 and $\text{N}(\text{CH}_3)_2$ groups in the compounds at equilibrium are listed in Table I. Only the relative areas of the various CH_3Si and CH_3P peaks were used for the quantitative determination of the molecular species. The experimental error of the relative area of each peak

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Table I. Proton Nmr Chemical Shifts^a of Methyl Groups Observed in Equilibrated Mixtures in Systems (CH₃)₂SiZ₂ vs. QT₂

Z	T	Q	Me ₂ SiZ ₂	Me ₂ SiZT	Me ₂ SiT ₂	QZ ₂	QTZ	ZT ₂
Cl	Br	CH ₃ P	-0.783	-0.930	-1.087	-2.215 (17.3)	-2.454 (18.6)	-2.700 (19.6)
Cl	Br	CH ₃ P(O)	-0.792	-0.933	-1.088	-2.500 (16.0)	-2.671 (15.5)	-2.867 (15.0)
Cl	Br	CH ₃ P(S)	-0.812	-0.963	-1.125	-2.861 (14.3)	-3.042 (14.0)	-3.256 (13.7)
Cl	OC ₆ H ₅	CH ₃ P	-0.530	-0.415	-0.273	-1.738 (17.4)	-1.658 (13.8)	-1.377 (10.5)
Cl	OC ₆ H ₅	CH ₃ P(O)	-0.636	-0.469	<i>b</i>	<i>b</i>	-1.899 (16.9)	-1.253 (17.8)
Br	OC ₆ H ₅	CH ₃ P(O)	-0.932	-0.604	<i>b</i>	<i>b</i>	-2.054 (16.5)	-1.569 (17.3)
Cl	OC ₆ H ₅	CH ₃ P(S)	-0.648	-0.489	-0.325	-2.471 (14.2)	-2.252 (15.0)	-1.995 (15.8)
Cl	SCH ₃	CH ₃ P(S)	-0.792	-0.648 ^c	-0.477 ^d	-2.808 (14.0)	-2.525 ^e (13.0)	-2.200 ^f (12.7)
Cl ^g	N(CH ₃) ₂	CH ₃ P	-0.508	-0.300 ^h	-0.052 ⁱ	-1.691 (18.0)	-1.450 ^j (11.0)	<i>b</i>
Cl ^g	N(CH ₃) ₂	CH ₃ P(O)	-0.633	-0.408 ^k	+0.017 ^l	-2.479 (10.0)	-1.792 ^m (16.0)	-1.263 ⁿ (15.5)
Cl	N(CH ₃) ₂	CH ₃ P(S)	-0.798	-0.428 ^o	-0.028 ^p	-2.797 (15.0)	-2.238 ^q (14.0)	-1.658 ^r (13.2)

^a In ppm relative to internal tetramethylsilane as measured in the neat liquid samples. The data listed in parentheses are ¹H-³¹P spin-spin coupling constants, *J*, in hertz. ^b Not observed at equilibrium. ^c CH₃S: -2.067. ^d CH₃S: -1.978. ^e CH₃S: -2.517 (*J* = 18.2). ^f CH₃S: -2.300 (*J* = 16). ^g The chemical shifts were measured in benzene solution. ^h N(CH₃)₂: -2.325. ⁱ N(CH₃)₂: -2.281. ^j N(CH₃)₂: -2.425 (*J* = 13.8). ^k N(CH₃)₂: -2.546. ^l N(CH₃)₂: -2.496. ^m N(CH₃)₂: -2.478 (*J* = 13.8). ⁿ N(CH₃)₂: -2.596 (*J* = 9.5). ^o N(CH₃)₂: -2.467. ^p N(CH₃)₂: -2.433. ^q N(CH₃)₂: -2.774 (*J* = 18.8). ^r N(CH₃)₂: -2.501 (*J* = 12.1).

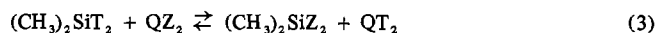
measured is about 1% of the total methyl groups directly attached to silicon and phosphorus.

The mixtures to be equilibrated were made up of various proportions of the neat reagents (CH₃)₂SiZ₂ and QT₂, where Z and T are the different monofunctional exchangeable substituents and Q is a non-exchangeable moiety based on methylphosphorus. For the various combinations of the two reagents, the reaction conditions at which the equilibrium data were obtained are the following, with the approximate time to reach equilibrium at the same temperature being given in parentheses: (CH₃)₂SiBr₂-CH₃PCl₂, 28 days at room temperature (5 days); (CH₃)₂SiBr₂-CH₃P(O)Cl₂, 167 hr at 120° (<75 hr); (CH₃)₂SiBr₂-CH₃P(S)Cl₂, 13 days at 120° (<10 days); (CH₃)₂Si(OC₆H₅)₂-CH₃PCl₂, 6 days at room temperature (15 hr); (CH₃)₂SiCl₂-CH₃P(O)(OC₆H₅)₂, 316 hr at 150° (113 hr); (CH₃)₂SiBr₂-CH₃P(O)(OC₆H₅)₂, 315 hr at 150° (113 hr); (CH₃)₂Si(OC₆H₅)₂-CH₃P(S)Cl₂, 17 days at 200° (<12 days); (CH₃)₂Si(SCH₃)₂-CH₃P(S)Cl₂, 19 days at 120° (<12 days); (CH₃)₂Si[N(CH₃)₂]₂-CH₃PCl₂, 5 days at room temperature in benzene as solvent (<3 days); (CH₃)₂Si[N(CH₃)₂]₂-CH₃P(O)Cl₂, 39 hr at 120° (<24 hr); (CH₃)₂Si[N(CH₃)₂]₂-CH₃P(S)Cl₂, 39 hr at 120° (<24 hr).

The rates of equilibration of the reagents in samples which were held at elevated temperatures are quite slow at room temperature. Therefore, upon quenching the samples to room temperature and obtaining the nmr spectra at this temperature, the equilibria still correspond to the elevated temperature at which the samples were held.

Results and Conclusions

Equilibria. A minimum of three equilibrium equations is required to describe completely the scrambling of two kinds of monofunctional substituents between two kinds of difunctional central moieties. Although this minimum number of equilibria may be expressed in various ways, we have chosen the following set of equations (where the exchanging monofunctional substituents are represented by Z and T and the methylphosphorus moiety is represented by Q).



Although the equilibrium of eq 3 is the one of particular interest here since it describes the distribution of Z and T between the two kinds of central moieties (CH₃)₂Si and Q, the equilibria of eq 1 and 2 also must be considered. These two

equations deal with the distribution of Z and T on either the dimethylsilicon or the methylphosphorus moiety, and each may be determined independently on the appropriate all-dimethylsilicon or all-methylphosphorus subsystem.

The overall equilibrium may be described quantitatively by the following set of three equilibrium constants corresponding to the reactions of eq 1-3.

$$K_{\text{Si}} = [(\text{CH}_3)_2\text{SiZ}_2][(\text{CH}_3)_2\text{SiT}_2] / [(\text{CH}_3)_2\text{SiZT}]^2 \quad (4)$$

$$K_{\text{Q}} = [\text{QZ}_2][\text{QT}_2] / [\text{QZT}]^2 \quad (5)$$

$$K_{\text{I}} = [(\text{CH}_3)_2\text{SiZ}_2][\text{QT}_2] / [(\text{CH}_3)_2\text{SiT}_2][\text{QZ}_2] \quad (6)$$

Values for these constants—the two “subsystem constants” *K*_{Si} and *K*_Q and the “intersystem constant” *K*_I—have been obtained in a number of cases from the experimental proton nmr data and are listed in Table II. In this table it is seen that the subsystem equilibrium constants as determined in the (CH₃)₂SiT₂-QZ₂ system agree quite well with the values of these same constants in those cases where they were determined separately in the systems (CH₃)₂SiZ₂-(CH₃)₂SiT₂ or QZ₂-QT₂ (see values listed in brackets in Table II).

Both subsystem equilibrium constants, *K*_{Si} as well as *K*_Q, are close to the ideal random value of 0.250 for the monofunctional substituents being chlorine and bromine. Deviations from randomness are seen for the exchange equilibria involving (1) chlorine or bromine atoms with phenoxy groups, (2) chlorine and methylthio groups, and (3) chlorine and dimethylamino groups, with the constants in the latter case being very small. All of the intersystem constants *K*_I in Table II were found to deviate considerably from the random value of 1.00. Deviations from randomness of *K*_I means that at equilibrium there is a preference of attachment of the monofunctional substituents to one of the central moieties. If this constant is larger than 1.00, the substituent Z in Table II at equilibrium is preferentially associated with the dimethylsilicon moiety and the substituent T with the methylphosphorus moiety. For values of *K*_I smaller than 1.00, the reverse situation is to be found. Table II also shows that for the same pair of substituents the intersystem

Table II. Equilibrium Constants^a for Substituent Exchange between Dimethylsilicon and Methylphosphorus Moieties in Systems (CH₃)₂SiZ₂ vs. QT₂

Z	T	Q	K _{Si}	K _Q	K _I
Cl ^b	Br	CH ₃ P	(3.18 ± 0.13) × 10 ⁻¹	(3.05 ± 0.13) × 10 ⁻¹	(5.87 ± 3.55) × 10 ³
			[(3.05 ± 0.26) × 10 ⁻¹] ^c	[(4.02 ± 0.38) × 10 ⁻¹] ^d	
Cl ^e	Br	CH ₃ P(O)	(3.21 ± 0.12) × 10 ⁻¹	(3.46 ± 0.13) × 10 ⁻¹	11.4 ± 1.4
Cl ^f	Br	CH ₃ P(S)	(3.07 ± 0.13) × 10 ⁻¹	(3.00 ± 0.11) × 10 ⁻¹	51.8 ± 6.8
Cl ^b	OC ₆ H ₅	CH ₃ P	(9.63 ± 0.76) × 10 ⁻²	(4.22 ± 0.58) × 10 ⁻²	(3.86 ± 0.48) × 10 ⁻²
			[(1.64 ± 0.11) × 10 ⁻¹] ^h		
Cl ^e	OC ₆ H ₅	CH ₃ P(O)		[(2.95 ± 0.34) × 10 ⁻¹] ^d	(1.49 ± 0.81) × 10 ⁵
Br ^e	OC ₆ H ₅	CH ₃ P(O)			(8.14 ± 3.82) × 10 ⁴
			[(1.35 ± 0.10) × 10 ⁻¹] ^h		
Cl ^g	OC ₆ H ₅	CH ₃ P(S)	(1.17 ± 0.05) × 10 ⁻¹	(1.03 ± 0.01) × 10 ⁻¹	(1.27 ± 0.20) × 10 ⁴
Cl ^f	SCH ₃	CH ₃ P(S)	(1.54 ± 0.08) × 10 ⁻¹	(2.06 ± 0.06) × 10 ⁻¹	(1.0 ± 3.0) × 10 ⁶
			[(1.78 ± 0.17) × 10 ⁻¹] ^h		
Cl ^b	N(CH ₃) ₂	CH ₃ P			(1.0 ± 1.3) × 10 ⁻²
			[(1.5 ± 1.6) × 10 ⁻⁴] ⁱ	[1 × 10 ⁻¹⁰] ^j	
Cl ^f	N(CH ₃) ₂	CH ₃ P(O)	(7.52 ± 24) × 10 ⁻⁴	(1.62 ± 1.05) × 10 ⁻³	(5.13 ± 4.47) × 10 ⁴
Cl ^f	N(CH ₃) ₂	CH ₃ P(S)			(1.0 ± 10) × 10 ¹⁵
				[(1.0 ± 0.5) × 10 ⁻⁴] ^d	
Ideal randomness			0.250	0.250	1.00

^a The constants not in brackets were obtained from the data in systems (CH₃)₂SiZ₂ vs. QT₂. The constants listed in brackets were obtained from separate studies of the system (CH₃)₂SiZ₂ vs. (CH₃)₂SiT₂ or QZ₂ vs. QT₂. ^b Constants correspond to room temperature. ^c Reference 2. ^d Reference 21. ^e Constants correspond to 150°. ^f Constants correspond to 120°. ^g Constants correspond to 200°. ^h Reference 3. ⁱ Reference 19. ^j Reference 20. ^k K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 7, 2105 (1968).

Table III. Equilibrium Constants^a for Substituent Exchange between Dimethylsilicon and Methylphosphorus Moieties in Systems (CH₃)₂SiZ₂ vs. QT at 120°

Z	T	Q = CH ₃ P<	Q = CH ₃ P(O)<	Q = CH ₃ P(S)<
Cl	Br	7.3 × 10 ² (K _A)	15.1 (K _B)	51.8 (K _C)
Cl	OPh	8.0 × 10 ⁻² (K _D)	4.0 × 10 ⁵ (K _E)	9.7 × 10 ⁶ (K _G)
Cl	SMe			1 × 10 ⁶ (K _H)
Cl	NMe ₂	3.2 × 10 ⁻² (K _J)	5.1 × 10 ⁴ (K _K)	1 × 10 ¹⁵ (K _L)
Br	OPh	1.1 × 10 ⁻⁴ (K _D /K _A)	1.9 × 10 ⁵ (K _F)	1.9 × 10 ³ (K _G /K _C)
Br	SMe			1.9 × 10 ⁴ (K _H /K _C)
Br	NMe ₂	4.4 × 10 ⁻⁵ (K _J /K _A)	3.4 × 10 ³ (K _K /K _B)	1.9 × 10 ¹³ (K _L /K _C)
OPh	SMe			10.3 (K _H /K _G)
OPh	NMe ₂	0.39 (K _J /K _D)	2.7 × 10 ⁻² (K _K /K _E)	1 × 10 ¹⁰ (K _L /K _G)
SMe	NMe ₂			1 × 10 ⁹ (K _L /K _H)

^a K_I = [(CH₃)₂SiZ₂][QT₂]/[(CH₃)₂SiT₂][QZ₂] (eq 6); constants in boldface type are experimental values from Table II, corrected to 120° where necessary; the other constants were estimated from the experimental ones as described.

constant depends greatly on the nature of the methylphosphorus moiety, whether the latter is a methylphosphinidene group, CH₃P<, a methylphosphonyl group, CH₃P(O)<, or a methylthiophosphonyl group, CH₃P(S)<.

For the exchanging substituents being chlorine and bromine atoms, the intersystem constants for all three cases are >1.00 but decrease in the order Q = CH₃P ≫ CH₃P(S) > CH₃P(O). For the pair of substituents being chlorine and phenoxy groups, K_I is smaller than 1.00 for Q = CH₃P; while, for Q = CH₃P(O) and CH₃P(S), it is considerably larger than 1.00—indicating in the latter two cases preference at equilibrium for the chlorine atoms to be on the methylsilicon moiety. For Q = CH₃P(O), the intersystem constant for the exchange of bromine atoms with phenoxy groups is very similar to the one for the analogous equilibria involving chlorine atoms. Attempts to determine intersystem constants for the scrambling of methoxyl groups with chlorine atoms between the central moieties used in this study were unsuccessful due to irreversible side reactions leading to the formation of methyl chloride and condensed species.¹⁸ Side reactions were also observed for the central moieties Q = CH₃P or CH₃P(O) when methylthio groups were scrambled with halogen atoms. However, no side reactions were observed for the same pair of substituents for Q = CH₃P(S) and the intersystem constant K_I was found to be very large. For the equilibria involving

the exchange of chlorine atoms and dimethylamino groups, K_I is smaller than 1.00 for Q = CH₃P, considerably larger than the random value for Q = CH₃P(O), and still larger for Q = CH₃P(S).

The equilibrium constants K_{Si}, K_Q, and K_I which for each system have been determined from a set of compositions at equilibrium (detailed analyses shown in Table A, which appears only in the microfilm edition of this journal) may now be used to compute the theoretical equilibrium distribution of all species participating in the equilibrium. This has been done for the compositions for which experimental data were obtained. These data and the computed equilibrium distributions corresponding to respective experimentally determined distributions are listed in parentheses in Table A.¹⁹

Although in most of the cases all three equilibrium constants could be determined directly from the experimental data of this paper, in some of the systems an insufficient number of species was seen at equilibrium to permit determination of K_{Si} or K_Q or both from these data. In such cases, the calculation of the theoretical equilibrium distributions was performed with values of the missing constants which were determined in separate studies^{2,3,20-22} and which are

(19) See paragraph at end of paper regarding supplementary material.

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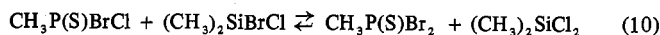
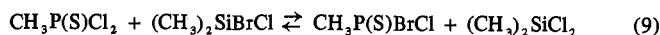
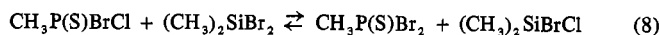
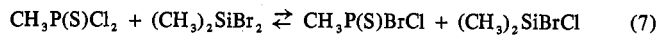
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listed in brackets in Table II. For $Z = \text{Br}$, $T = \text{OC}_6\text{H}_5$, and $Q = \text{CH}_3\text{P}(\text{O})$ the constant K_Q could not be determined from the present experimental data nor was it known from a separate study as in the other cases. For the calculations K_Q was therefore assumed to have the same value as that for the analogous chlorine system, $Z = \text{Cl}$. Inspection of the data in Table A shows a good match of experimental and calculated equilibrium concentrations, indicating that the equilibria are well represented by the constants of Table II.

The various reaction rates for the range of systems described in this paper required that the study of the redistribution equilibria be carried out at different temperatures. In Table III all of the intersystem equilibrium constants, K_I , that were determined at a temperature other than 120° were converted to this temperature and they have been individually identified by subscripts (K_A through K_L). The temperature conversion was performed on the assumption that the entire entropy of the reaction is attributable to scrambling. With the experimentally derived constants we may now estimate additional equilibrium constants for systems that were not investigated but for which equilibrium constants may be derived from simple stoichiometric considerations from the ones studied. These new intersystem equilibrium constants are reported in Table III along with the ratios of the experimentally derived constants from which these new constants were obtained.

These indirectly obtained constants show that for the substituents Br and OC_6H_5 the intersystem constants decrease in the order $\text{CH}_3\text{P}(\text{O}) > \text{CH}_3\text{P}(\text{S}) > \text{CH}_3\text{P}$ which is similar to the order for the pair Cl and OC_6H_5 . For the pair of substituents Br and $\text{N}(\text{CH}_3)_2$ a similar pattern is seen as for Cl and $\text{N}(\text{CH}_3)_2$, described above. For the exchange of OC_6H_5 with $\text{N}(\text{CH}_3)_2$ groups, the estimated intersystem equilibrium constants decrease in the order $\text{CH}_3\text{P}(\text{S}) > \text{CH}_3\text{P} > \text{CH}_3\text{P}(\text{O})$.

Kinetic Measurements. The rate data for the exchange of Br and Cl between the $(\text{CH}_3)_2\text{Si}<$ and $\text{CH}_3\text{P}(\text{S})<$ moieties are presented in Figure 1, which shows how these molecular species change with time. On the assumption that the reactions occur between pairs of molecules, we have the following set of six equations which are involved in the equilibration.



For the data shown on the left-hand side of Figure 1, it is apparent that the initial rate process must be associated with the forward reaction of eq 7, which from the initial slope would exhibit a rate constant of *ca.* $4.3 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ if

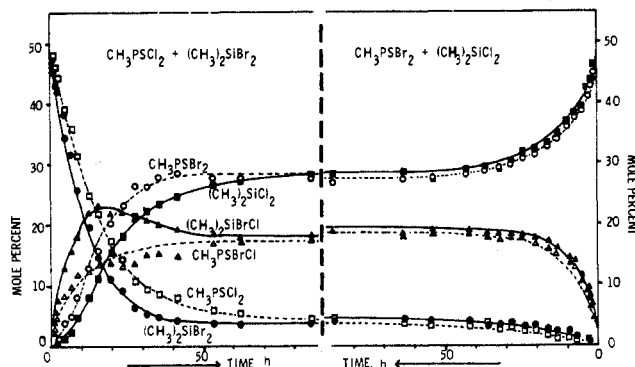


Figure 1. Kinetic curves for the forward and reverse reactions for the exchange of chlorine and bromine atoms between the $\text{CH}_3\text{P}(\text{S})<$ and $(\text{CH}_3)_2\text{Si}<$ moieties at 120° . These curves correspond to equimolar quantities of the reagents shown.

the reaction were first order in each reagent. This reaction is immediately followed by the forward reactions of eq 8 and 9, with eq 10 also contributing. The maximum in the concentration of $(\text{CH}_3)_2\text{SiBrCl}$ occurs because the forward reaction of eq 8 is more rapid than that of eq 9. On the assumption that order equals molecularity, the forward rate constants of eq 8 and 9 would be respectively somewhat more than 2 and less than 1 times that of eq 7. For the data shown on the right-hand side of Figure 1, the initial rate process is associated with the reverse reaction of eq 10. This is followed by the reverse reactions of eq 8, 9, and then 7. For order equaling molecularity, the reverse reaction of eq 10 would exhibit a rate constant of *ca.* $5 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ from the initial slope, with the reverse reactions of eq 8 and 9 being about one-third as fast as that of the reverse of eq 10.

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Registry No. $(\text{CH}_3)_2\text{SiBr}_2$, 4095-10-7; CH_3PCl_2 , 676-83-5; $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$, 676-97-1; $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$, 676-98-2; $(\text{CH}_3)_2\text{Si}(\text{OC}_6\text{H}_5)_2$, 3440-02-6; $(\text{CH}_3)_2\text{SiCl}_2$, 75-78-5; $\text{CH}_3\text{P}(\text{O})(\text{OC}_6\text{H}_5)_2$, 7526-26-3; $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$, 3860-91-1; $(\text{CH}_3)_2\text{Si}[\text{N}(\text{CH}_3)_2]_2$, 3768-58-9.

Supplementary Material Available. Table A giving the equilibrium data for all systems studied will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2856.