

Halogen–Halogen Exchange Equilibria between Dimethylgermanium and Various Methylphosphorus Moieties

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Equilibrium constants were determined experimentally for the redistribution of the pairs of substituents Cl/Br, Cl/I and Br/I between the $(\text{CH}_3)_2\text{Ge}$ and various methylphosphorus moieties $[\text{CH}_3\text{P}(\text{O})$ and $\text{CH}_3\text{P}(\text{S})]$ using quantitative proton nuclear magnetic resonance to assay the equilibrated mixtures. By simple stoichiometric computations, additional equilibrium constants were calculated for the pairs of substituents Cl/SCH₃, Br/SCH₃, Cl/OC₆H₅ and Br/OC₆H₅.

Introduction

As has been shown previously in a series of studies^{1,2} from this laboratory, competition (redistribution) equilibria of pairs of exchangeable, monofunctional substituents between two kinds of poly-functional central moieties generally are nonrandom. This means that at equilibrium, a preference is displayed in the distribution of the pair of substituents between the two central moieties. In this paper, such equilibria are reported for the central moieties being dimethylgermanium and various methylphosphorus groups and pairs of halogens. These studies are closely related to earlier studies of corresponding equilibria^{3,4} between methylgermanium and various methylphosphorus moieties as well as to similar equilibria between the latter moieties with dimethylsilicon.⁵

Experimental

Reagents

The dimethyldihalogermanes,⁶ methylphosphonous dichloride,⁷ methylphosphonyl dichloride⁸ and methylphosphonothioic dichloride⁹ were prepared by literature methods. Methylphosphonous dibromide¹⁰ and methylphosphonothioic dibromide¹¹ were obtained from Dr. L. Maier.

Data Acquisition

Sample preparation, equilibration, quantitative assay of the species present at equilibrium by proton nmr

(Varian A60) and calculation of weighted-average equilibrium constants and theoretical equilibrium compositions were performed as reported previously.^{12,13} The pairs of reagents used to make up the sets of samples to be equilibrated are shown as subheadings in Table I which summarizes the equilibrium compositions studied. The proton nmr chemical shifts of the signals of the methyl groups of the species seen at equilibrium are listed in Table II, with the peak areas of these groups representing their relative concentration. The experimental error of the relative area of each peak measured by electronic integration is about 1% of the total area of all methyl groups in a sample.

For the various combinations of the two neat reagents of Table I, 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. System A: 20 d (8 d) at room temperature; due to line broadening of the CH₃P signals the spectra were measured after equilibration in samples diluted with 1 part of CCl₄. System B: 25 d (13 d) at 120°C. System C: 13 d (4 d) at 120°C; spectra were measured after equilibration in samples diluted with 3 parts of CCl₄. System D: 15 d (2 d) at room temperature; due to line broadening, the spectra were obtained at room temperature upon dilution with 5 parts of CCl₄. Spectra were also obtained neat at –30°C probe temperature. System E: 3 d (0.5 d) at room temperature; due to line broadening in the region of the CH₃P resonances, the spectra were measured after dilution with 5 parts of CCl₄. System G: 1 d (7 d) at room temperature.

In all systems, the rates of equilibration involving transfer of exchangeable substituents from dimethylgermanium to methylphosphorus (CH₃P) and vice versa, as well as from dimethylgermanium to dimethylgermanium and from methylphosphorus (CH₃P) to methylphosphorus (CH₃P) are rapid at room temperature so that such equilibria will correspond to the temperature of the probe of the spectrometer. The rates of equilibration involving transfer of substituents from CH₃P(O) or CH₃P(S) to germanium and vice versa, as well as transfer from phosphorus to phosphorus in these systems is quite slow at room temper-

TABLE I. Equilibrium Data in Mol Percent in Systems $(\text{CH}_3)_2\text{GeI}_2$ vs. QZ_2 where I and Z are Monofunctional Exchangeable Substituents and Q is a Methylphosphorus Moiety.

A. System $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ vs. $(\text{CH}_3)_2\text{GeBr}_2$					
$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$	$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$	CH_3PBrCl	$\text{CH}_3\text{P}(\text{O})\text{Cl}_2$	$(\text{CH}_3)_2\text{GeBr}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.237 ^a	0.881 ^a	2.0	0.1	72.6	0.9
(0.207) ^c	(0.902) ^c	(3.1)	(0.4)	(69.4)	(1.3)
0.469	0.766	8.7	1.9	48.9	3.8
(0.452)	(0.778)	(9.3)	(2.2)	(47.3)	(3.9)
0.699	0.651	15.1	5.7	33.1	6.0
(0.662)	(0.668)	(16.0)	(6.4)	(30.9)	(6.9)
0.938 ^e	0.531	22.0	13.4	19.3	9.9
(0.928)	(0.534)	(22.1)	(13.6)	(18.4)	(9.7)
1.141	0.430	24.6	22.4	11.4	11.9
(1.129)	(0.430)	(25.5)	(22.4)	(10.7)	(11.5)
1.373	0.314	27.0	35.4	4.7	11.6
(1.357)	(0.310)	(26.5)	(36.0)	(4.8)	(12.2)
1.610	0.195	23.4	53.6	1.5	10.8
(1.597)	(0.198)	(22.9)	(54.5)	(1.4)	(10.9)
B. System $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ vs. $(\text{CH}_3)_2\text{GeBr}_2$					
$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$	$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$	$\text{CH}_3\text{P}(\text{O})\text{BrCl}$	$\text{CH}_3\text{P}(\text{O})\text{Cl}_2$	$(\text{CH}_3)_2\text{GeBr}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.239 ^a	0.881 ^a	3.9	4.9	82.2	0.1
(0.218) ^c	(0.902) ^c	(5.5)	(5.3)	(80.4)	(0.2)
0.465	0.767	7.0	13.0	69.0	0.2
(0.435)	(0.793)	(8.6)	(13.6)	(66.2)	(0.3)
0.721	0.640	9.4	24.6	52.6	0.6
(0.715)	(0.649)	(10.7)	(24.4)	(51.9)	(0.5)
0.961 ^e	0.519	11.5	35.1	40.9	0.6
(0.936)	(0.522)	(11.6)	(35.6)	(39.5)	(0.7)
1.200	0.400	11.3	44.2	30.7	1.0
(1.134)	(0.434)	(11.7)	(47.7)	(28.0)	(0.9)
1.443	0.279	10.5	61.1	17.0	1.1
(1.446)	(0.278)	(10.8)	(60.9)	(17.3)	(1.1)
1.685	0.152	8.8	75.7	7.1	1.3
(1.692)	(0.148)	(9.1)	(75.5)	(7.8)	(1.1)
C. System $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ vs. $(\text{CH}_3)_2\text{GeBr}_2$					
$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$	$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$	$\text{CH}_3\text{P}(\text{S})\text{BrCl}$	$\text{CH}_3\text{P}(\text{S})\text{Cl}_2$	$(\text{CH}_3)_2\text{GeBr}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.245 ^a	0.878 ^a	5.3	1.5	74.2	0.7
(0.234) ^c	(0.886) ^c	(5.3)	(1.7)	(72.9)	(0.8)
0.488	0.756	11.2	6.3	54.9	2.0
(0.475)	(0.766)	(11.4)	(6.9)	(54.1)	(2.1)

D1. ^f System CH_3PCl_2 vs. $(\text{CH}_3)_2\text{GeI}_2$		$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$		$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$		CH_3PI_2	CH_3PCl_2	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.726	0.637	6.1	15.6	14.5	39.4	21.0	3.4			
(0.724)	(0.638)	(5.8)	(16.2)	(14.3)	(39.4)	(20.9)	(3.4)			
0.962 ^e	0.519	4.7	18.9	24.2	27.5	20.0	4.7			
(0.967)	(0.522)	(5.0)	(19.3)	(23.8)	(27.2)	(20.1)	(4.6)			
1.195	0.402	3.8	20.7	34.7	17.7	17.6	5.6			
(1.189)	(0.409)	(3.9)	(20.7)	(35.2)	(17.2)	(17.5)	(5.5)			
1.438	0.281	2.3	19.6	49.6	9.3	13.4	5.8			
(1.438)	(0.285)	(2.6)	(20.0)	(49.3)	(8.9)	(13.2)	(6.0)			
1.646	0.177	1.6	17.2	63.8	3.6	8.4	5.5			
(1.642)	(0.175)	(1.4)	(17.0)	(63.9)	(3.7)	(8.3)	(5.7)			
D2. ^g System CH_3PCl_2 vs. $(\text{CH}_3)_2\text{GeI}_2$										
$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$		$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$		CH_3PI_2	CH_3PCl_2	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.600 ^a	0.700 ^a	25.6 ^b	2.6	—	—	31.3	25.2	15.3	—	—
(0.584) ^c	(0.718) ^c	(26.6) ^d	(2.8)	(0.6)	(0.6)	(30.0)	(24.2)	(15.9)	(0.6)	(0.6)
0.929	0.536	31.7	9.2	3.7	3.7	8.7	19.0	27.7	3.7	3.7
(0.910)	(0.554)	(32.5)	(8.9)	(5.1)	(5.1)	(8.2)	(16.9)	(28.5)	(5.1)	(5.1)
1.256 ^e	0.372	23.5	18.2	21.7	21.7	1.6	7.9	27.1	21.7	21.7
(1.237)	(0.366)	(24.3)	(16.1)	(22.4)	(22.4)	(1.4)	(7.0)	(28.8)	(22.4)	(22.4)
1.526	0.237	12.8	18.4	43.9	43.9	0.1	3.2	21.5	43.9	43.9
(1.524)	(0.248)	(13.5)	(17.2)	(45.6)	(45.6)	(0.3)	(2.6)	(20.8)	(45.6)	(45.6)
1.807	0.097	3.5	11.0	75.3	75.3	—	0.6	9.7	75.3	75.3
(1.816)	(0.103)	(3.7)	(11.5)	(75.2)	(75.2)	(0.0)	(0.5)	(9.2)	(75.2)	(75.2)
D2. ^g System CH_3PCl_2 vs. $(\text{CH}_3)_2\text{GeI}_2$										
$R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$		$R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$		CH_3PI_2	CH_3PCl_2	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}_2$
0.600 ^a	0.700 ^a	27.7 ^b	1.5	0.4	0.4	29.7	24.4	16.2	0.4	0.4
(0.591) ^c	(0.703) ^c	(28.1) ^d	(1.7)	(0.2)	(0.2)	(28.9)	(24.4)	(16.7)	(0.2)	(0.2)
0.929	0.536	39.3	5.7	1.8	1.8	5.4	14.7	33.2	1.8	1.8
(0.904)	(0.533)	(36.6)	(7.0)	(2.8)	(2.8)	(5.8)	(15.2)	(32.5)	(2.8)	(2.8)
1.256 ^e	0.372	27.4	16.3	19.0	19.0	0.4	4.5	32.4	19.0	19.0
(1.236)	(0.373)	(26.3)	(16.0)	(20.5)	(20.5)	(0.6)	(4.7)	(32.0)	(20.5)	(20.5)
1.526	0.237	14.6	16.8	44.0	44.0	0.3	1.7	22.6	44.0	44.0
(1.517)	(0.246)	(14.1)	(17.4)	(44.8)	(44.8)	(0.1)	(1.6)	(22.0)	(44.8)	(44.8)
1.807	0.097	3.2	10.6	75.3	75.3	—	0.5	10.4	75.3	75.3
(1.825)	(0.109)	(3.7)	(11.6)	(75.0)	(75.0)	(0.0)	(0.3)	(9.4)	(75.0)	(75.0)

^a From the ingredients of the mixture as defined. ^b From the nmr data in mol. %.
^c Values in parentheses calculated from the corresponding nmr data. ^d Values in parentheses calculated from the equilibrium constants of Table III. ^e Compositions

in which the proton nmr chemical shifts in Table II were determined. ^f Nmr data were obtained at room temperature. ^g Nmr data were obtained at -30°C probe temperature.

TABLE I. (Cont.)

E. System $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ vs. $(\text{CH}_3)_2\text{GeI}_2$ $R \equiv [\text{Cl}]/([\text{Ge}] + [\text{P}])$ $R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$						
	$\text{CH}_3\text{P}(\text{S})\text{I}_2$	$\text{CH}_3\text{P}(\text{S})\text{ClI}$	$\text{CH}_3\text{P}(\text{S})\text{Cl}_2$	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeClI}$	$(\text{CH}_3)_2\text{GeCl}_2$
0.409 ^a	7.8 ^b	6.4	4.3	59.0	18.5	4.1
(0.417) ^c	(8.9) ^d	(7.0)	(4.5)	(58.3)	(17.5)	(3.7)
0.851	9.1	14.5	17.9	31.6	18.5	8.4
(0.856)	(9.5)	(14.7)	(18.3)	(31.3)	(18.5)	(7.6)
1.214 ^e	6.9	16.4	35.7	15.3	15.3	10.2
(1.235)	(7.5)	(18.0)	(35.2)	(15.6)	(14.4)	(9.3)
1.487	4.5	17.8	51.8	6.9	10.0	8.9
(1.492)	(5.0)	(17.8)	(51.5)	(7.0)	(9.5)	(9.1)
1.763	1.5	12.8	72.9	1.3	3.8	7.6
(1.776)	(2.0)	(13.3)	(72.9)	(1.4)	(3.7)	(6.7)
F. System CH_3PBr_2 vs. $(\text{CH}_3)_2\text{GeI}_2$ $R \equiv [\text{Br}]/([\text{Ge}] + [\text{P}])$ $R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$						
	CH_3PI_2	CH_3PBrI	CH_3PBr_2	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeBrI}$	$(\text{CH}_3)_2\text{GeBr}_2$
0.330 ^a	14.6 ^b	1.3	—	55.1	25.0	4.0
(0.343) ^c	(15.1) ^d	(1.2)	(0.0)	(55.7)	(24.3)	(3.7)
0.725	27.4	3.2	—	18.9	31.8	18.7
(0.724)	(27.1)	(7.7)	(0.6)	(18.8)	(29.5)	(16.2)
1.065 ^e	26.6	16.4	6.0	3.2	17.4	30.4
(1.066)	(26.2)	(19.6)	(4.4)	(4.5)	(18.5)	(26.8)
1.365	13.9	27.6	26.6	0.3	4.7	27.1
(1.397)	(12.7)	(31.9)	(23.6)	(0.4)	(5.4)	(26.0)
1.672	3.0	27.3	53.9	0.3	1.0	14.5
(1.651)	(3.3)	(25.0)	(55.3)	(0.0)	(1.1)	(15.3)
G. System $\text{CH}_3\text{P}(\text{S})\text{Br}_2$ vs. $(\text{CH}_3)_2\text{GeI}_2$ $R \equiv [\text{Br}]/([\text{Ge}] + [\text{P}])$ $R' \equiv [\text{Ge}]/([\text{Ge}] + [\text{P}])$						
	$\text{CH}_3\text{P}(\text{S})\text{I}_2$	$\text{CH}_3\text{P}(\text{S})\text{BrI}$	$\text{CH}_3\text{P}(\text{S})\text{Br}_2$	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeBrI}$	$(\text{CH}_3)_2\text{GeBr}_2$
1.801 ^a	1.1 ^b	15.9	65.6	—	1.9	15.5
(1.800) ^c	(1.5) ^d	(15.2)	(66.5)	(0.1)	(1.7)	(15.2)
1.522	6.9	24.0	38.5	0.9	7.9	23.2
(1.553)	(7.0)	(24.7)	(37.0)	(0.9)	(7.4)	(23.1)
1.170 ^e	15.7	23.9	14.4	5.0	18.0	23.0
(1.167)	(15.8)	(23.1)	(14.4)	(5.1)	(18.1)	(23.5)
0.773	19.1	11.6	3.6	22.4	29.0	15.5
(0.788)	(19.8)	(11.5)	(2.9)	(21.0)	(29.5)	(15.3)
0.384	14.0	3.1	—	54.0	26.2	3.8
(0.369)	(13.3)	(2.7)	(0.2)	(53.2)	(25.9)	(4.7)

For Footnotes see page 207.

TABLE II. Proton NMR Chemical Shifts of Methyl Groups Observed in Equilibrated Mixtures in Systems $(\text{CH}_3)_2\text{GeT}_2$ vs. QZ_2 .

Z	T	Q	$(\text{CH}_3)_2\text{GeT}_2$	$(\text{CH}_3)_2\text{GeZT}$	$(\text{CH}_3)_2\text{GeZ}_2$	QT_2	QZT	QZ_2
Cl ^b	Br	CH ₃ P	1.450	1.317	1.175	2.675 (19.5)	2.430 (18.6)	2.188 (17.5)
Cl ^c	Br	CH ₃ P(O)	1.462	1.321	1.188	2.882 (14.8)	2.627 (15.6)	2.457 (16.1)
Cl ^c	Br	CH ₃ P(S)	1.462	1.323	1.188	3.150 (13.4)	2.949 (14.0)	2.769 (14.4)
Cl ^d	I	CH ₃ P	1.945	1.569	1.238	3.315 (20.2)	2.835 (19.2)	2.282 (17.1)
Cl	I	CH ₃ P(S)	1.888	1.529	1.214	3.771 (12.9)	3.223 (14.1)	2.791 (14.2)
Br ^e	I	CH ₃ P	1.890	1.630	1.465	3.266 (20.4)	3.006 (20.0)	2.713 (19.9)
Br	I	CH ₃ P(S)	1.913	1.703	1.504	3.785 (12.1)	3.466 (12.9)	3.209 (13.4)

^a Proton chemical shifts δ (TMS = 0) were determined in the neat equilibrated mixtures of Table I marked with the superscript e. Coupling constants $^2J_{\text{HP}}$ in Hz are listed in parentheses. ^b In 1 : 1 CCl₄. ^c In 1 : 3 CCl₄. ^d At -30° C. ^e In 1 : 5 CCl₄.

ature.^{5,14} Therefore, these samples upon quenching to room temperature from 120° C and obtaining the nmr spectra subsequently at this temperature, will, as far as the above exchanges are concerned, represent the equilibria corresponding to the elevated temperature at which these samples were held. Methyl groups directly attached to Ge or P under the present experimental conditions do not participate in the exchange processes.

Results and Discussion

Equilibrium Constants

The comprehensive mathematical treatment of redistribution equilibria of the type where pairs of monofunctional, exchangeable substituents are exchanging between two kinds of difunctional central moieties requires a minimum of three equilibrium constants. These are expressed by the following set of constants:

$$K_{\text{Ge}} = \frac{[(\text{CH}_3)_2\text{GeT}_2][(\text{CH}_3)_2\text{GeZ}_2]}{[\text{CH}_3]_2 \text{GeTZ}}^2 \quad (1)$$

$$K_{\text{Q}} = \frac{[\text{QT}_2][\text{QZ}_2]}{[\text{QTZ}]^2} \quad (2)$$

$$K_{\text{I(Ge/P)}} = \frac{[(\text{CH}_3)_2\text{GeZ}_2][\text{QT}_2]}{\{[(\text{CH}_3)_2 \text{GeT}_2][\text{QZ}_2]\}} \quad (3)$$

Of these, the constants K_{Ge} and K_{Q} – the subsystem constants – determine the equilibria of the two substituents on each of the central moieties. The constant $K_{\text{I(Ge/P)}}$ – the intersystem constant – is the one of particular interest here since it determines the distribution of the two kinds of substituents between the two

kinds of central moieties. Experimentally determined values for the constants K_{Ge} , K_{Q} and $K_{\text{I(Ge/P)}}$ from the nmr data in Table I are summarized in Table III. The values of K_{Ge} and K_{Q} for the various systems listed in Table III agree quite well with values of the same constants obtained previously in separate studies^{14–16} confirming that halogen-halogen exchanges on the germanium as well as the phosphorus moieties generally are close to the ideal random case, except for the Cl/I exchange where small but significant deviations are observed. All intersystem constants deviate from the random value $K_{\text{I(rand)}} = 1.00$, although the deviations in the majority of the cases in Table III are not very large. Deviation from randomness of $K_{\text{I(Ge/P)}}$ 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 III at equilibrium is preferentially associated with the dimethylgermanium moiety and the substituent T with the methylphosphorus moiety. For values of $K_{\text{I(Ge/P)}}$ smaller than 1.00, the reverse situation is found. The extent of the preference is proportional to the extent of the deviation from the random case.

The set of equilibrium constants in Table III which for each system have been determined from the set of compositions at equilibrium in Table I may now be used to compute the theoretical equilibrium distribution of all species participating in the equilibrium in a particular system. This has been done for the compositions for which experimental data were obtained. These data and the computed equilibrium distributions, the latter in parentheses, corresponding to the

TABLE III. Equilibrium Constants^a for Substituent Exchange between Dimethylgermanium and Methylphosphorus Moieties in Systems (CH₃)₂GeT₂ vs. QZ₂.

System	Z	T	Q	K _{Ge}	K _Q	K _{1(Ge/P)}
A ^b	Cl	Br	CH ₃ P	0.30±0.01 [0.30±0.02] ^e	0.31±0.01 [0.40±0.04] ^f	(4.4±0.6) × 10 ⁻¹
B ^c	Cl	Br	CH ₃ P(O)	0.21±0.05	0.21±0.05 [0.36±0.04] ^f	(4.3±0.6) × 10 ⁻⁴
C ^c	Cl	Br	CH ₃ P(S)	0.31±0.02	0.32±0.02 [0.36±0.04] ^f	(3.4±0.1) × 10 ⁻²
D1 ^b	Cl	I	CH ₃ P	0.72±0.03 [0.67±0.07] ^e	1.59±0.07	(2.3±0.6) × 10 ⁺¹
D2 ^d	Cl	I	CH ₃ P	0.81±0.04	2.09±0.10	(7.3±2.0) × 10 ⁺¹
E ^c	Cl	I	CH ₃ P(S)	0.70±0.04	0.81±0.05	(1.3±0.1) × 10 ⁻¹
F ^b	Br	I	CH ₃ P	0.35±0.03 [0.34±0.01] ^e	0.30±0.04	(3.6±0.8) × 10 ⁺¹
G ^b	Br	I	CH ₃ P(S)	0.37±0.02	0.42±0.02	5.0±0.4

^aThe equilibrium constants K_{Ge}, K_Q and K_{1(Ge/P)} are defined by eqs. (1), (2) and (3) in the text. ^bConstants correspond to room temperature. ^cConstants K_Q and K_{1(Ge/P)} correspond to 120° C, K_{Ge} to room temperature.

^dConstants correspond to -30° C. ^eLiterature values¹⁵ obtained separately in studies of the systems (CH₃)₂GeT₂ vs. (CH₃)₂GeZ₂. ^fLiterature values^{14, 16} obtained separately in studies of the systems QT₂ vs. QZ₂.

respective sample compositions are summarized in Table I. Agreement between experimental and calculated values generally is very good.

After conversion of the intersystem constants K_{1(Ge/P)} in Table III, where necessary, to 120° C (on the basis that the entire ΔS of the reaction equation is attributed to scrambling), these constants are now summarized in Table IV. In this tabulation it is seen that, with the exception of Systems D, F and G, the values of K_{1(Ge/P)} are smaller than one, indicating that at equilibrium the heavier halogen will favor the di-

methylgermanium moiety. The opposite is found for the equilibria in systems D, F and G. The data also indicate that the environment on the phosphorus atom exerts a significant effect on the competition equilibria of a given pair of substituents.

For a given pair of substituents, the intersystem 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)<.

TABLE IV. Intersystem Equilibrium Constants^a at 120° C.

System	Z	T	Q	K _{1(Ge/P)}	K _{1(Si/P)}
A	Cl	Br	CH ₃ P	0.54	7.3 × 10 ²
B	Cl	Br	CH ₃ P(O)	4.3 × 10 ⁻⁴	15.1
C	Cl	Br	CH ₃ P(S)	3.4 × 10 ⁻²	51.8
D	Cl	I	CH ₃ P	7.0	(5.8 × 10 ⁶)
E	Cl	I	CH ₃ P(S)	1.3 × 10 ⁻¹	(1.2 × 10 ⁴)
F	Br	I	CH ₃ P	15	(7.5 × 10 ⁴)
G	Br	I	CH ₃ P(S)	3.4	(1.7 × 10 ⁴)
(H)	Cl	SCH ₃	CH ₃ P(S)	(1 × 10 ³)	1 × 10 ⁶
(I)	Br	SCH ₃	CH ₃ P(S)	(8.6 × 10 ⁴)	1.9 × 10 ⁴
(J)	Cl	OC ₆ H ₅	CH ₃ P	(35)	8.0 × 10 ⁻²
(K)	Cl	OC ₆ H ₅	CH ₃ P(O)	(1.8 × 10 ⁸)	4 × 10 ⁵
(L)	Cl	OC ₆ H ₅	CH ₃ P(S)	(4.3 × 10 ⁷)	9.7 × 10 ⁴
(M)	Br	OC ₆ H ₅	CH ₃ P	(1.6 × 10 ²)	1.1 × 10 ⁻⁴
(N)	Br	OC ₆ H ₅	CH ₃ P(O)	(2.9 × 10 ¹¹)	1.9 × 10 ⁵
(O)	Br	OC ₆ H ₅	CH ₃ P(S)	(2.9 × 10 ⁹)	1.9 × 10 ³

^a K_{1(Ge/P)} is defined by equation (3); the values not in parentheses were determined in this paper and are converted to 120° C where necessary; the values in parentheses were calculated using equation (6). K_{1(Si/P)} = [(CH₃)₂SiZ₂][QT₂]/{[(CH₃)₂SiT₂][QZ₂]}; the values of K_{1(Si/P)} (at 120° C) not in parentheses were taken from reference 5; the values in parentheses were calculated according to equation (5).

For the exchanging substituents being chlorine and bromine atoms, the intersystem equilibrium constants for all three cases are smaller than 1.00, indicating that the various methylphosphorus moieties at equilibrium prefer bonding to chlorine over that to bromine atoms. Within this series the chlorine acceptor strength of phosphorus (*versus* that of dimethylgermanium) increases in the order $\text{CH}_3\text{P} < \text{CH}_3\text{P}(\text{S}) \ll \text{CH}_3\text{P}(\text{O})$. It is noteworthy to point out that in the related study⁵ of the equilibria between methylphosphorus and dimethylsilicon moieties, the situation is reversed – the methylphosphorus moieties at equilibrium, for the same pair of substituents, prefer bonding to bromine and the bromine acceptor strength increasing in the order $\text{CH}_3\text{P}(\text{O}) < \text{CH}_3\text{P}(\text{S}) < \text{CH}_3\text{P}$. The latter implies, of course, that the chlorine acceptor strength increases in the opposite order which is consistent with the above dimethylgermanium case.

For the exchanges of the pairs Cl/I and Br/I, the constants involving the $\text{CH}_3\text{P}(\text{O})$ moiety could not be obtained experimentally since mixtures of $(\text{CH}_3)_2\text{GeI}_2$ and $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ as well as $(\text{CH}_3)_2\text{GeI}_2$ and $\text{CH}_3\text{P}(\text{O})\text{Br}_2$ upon equilibration formed insoluble $\text{CH}_3\text{P}(\text{O})\text{I}_2$, for which no suitable solvent could be found. For the Cl/I exchanges in the remaining two systems, the order of chlorine acceptor strength is $\text{MeP} < \text{MeP}(\text{S})$. However, for CH_3P , the intersystem constant is larger than the random value, signaling preference at equilibrium of the dimethylgermanium moiety for iodine, whereas for $\text{CH}_3\text{P}(\text{S})$, the constant is smaller than 1.0 indicating a reversal of affinities between the halogens and the two central moieties. For the pair Br/I, both constants are larger than 1.0 indicating that, at equilibrium, the phosphorus moieties prefer bonding to iodine, with the iodine acceptor strength increasing from $\text{CH}_3\text{P}(\text{S})$ to CH_3P .

For the system CH_3PCl_2 vs. $(\text{CH}_3)_2\text{GeI}_2$, the equilibria have been determined at two temperatures. Since the rate of equilibration in this system is quite rapid at room temperature (line broadening¹⁴ was observed in the CH_3P region of the spectra), the data obtained at -30°C probe temperature correspond to the equilibrium at this temperature. The equilibrium constants obtained at both temperatures are reported in Table III. From the constants at the two temperatures, the enthalpy of the reaction corresponding to these equilibria has been calculated as $\Delta H = -1.3$ kcal.

Estimation of Additional Equilibrium Constants

The intersystem equilibrium constants $K_{\text{I}(\text{Ge}/\text{P})}$ for the dimethylgermanium/methylphosphorus systems (corrected to 120°C) listed in Table IV may now be compared with analogous constants for the dimethylsilicon/methylphosphorus system (at 120°C) reported earlier⁵ and also listed in Table IV. First, however, using simple stoichiometric calculations and the data of this paper in conjunction with the respective inter-

system constants of the dimethylsilicon/dimethylgermanium system^{13,15,17} defined by eq. (4),

$$K_{\text{I}(\text{Ge}/\text{Si})} = [(\text{CH}_3)_2\text{SiT}_2][(\text{CH}_3)_2\text{GeZ}_2] / \{[(\text{CH}_3)_2\text{SiZ}_2][(\text{CH}_3)_2\text{GeT}_2]\} \quad (4)$$

we may calculate the four constants $K_{\text{I}(\text{Si}/\text{P})}$ listed in Table IV in parentheses. These previously have not been determined experimentally. The stoichiometric relationship for these calculations is given below.

$$K_{\text{I}(\text{Si}/\text{P})} = K_{\text{I}(\text{Ge}/\text{P})} / K_{\text{I}(\text{Ge}/\text{Si})} = [(\text{CH}_3)_2\text{SiZ}_2][\text{QT}_2] / \{[(\text{CH}_3)_2\text{SiT}_2][\text{QZ}_2]\} \quad (5)$$

Equation (5) may also be used to calculate previously undetermined intersystem constants $K_{\text{I}(\text{Ge}/\text{P})}$ if, for a given pair of substituents, $K_{\text{I}(\text{Si}/\text{P})}$ and $K_{\text{I}(\text{Ge}/\text{Si})}$ are known. These computations, based on eq. (6)

$$K_{\text{I}(\text{Ge}/\text{P})} = K_{\text{I}(\text{Si}/\text{P})} \times K_{\text{I}(\text{Ge}/\text{Si})} \quad (6)$$

result in the $K_{\text{I}(\text{Ge}/\text{P})}$ values in Table IV listed in parentheses. Eq. (6) may also be used to calculate $K_{\text{I}(\text{Ge}/\text{P})}$ for systems for which experimental data are available in order to check the consistency of our data. Based on eq. (6) and using the appropriate constants, we obtained the following $K_{\text{I}(\text{Ge}/\text{P})}$ values (at 120°C), System A: 0.21; System B: 4.4×10^{-4} ; and System C: 1.5×10^{-2} . Upon comparison with the corresponding values in Table IV, it is seen that good agreement is obtained.

Another application of the relationship of eq. (6) is the following. In the course of this study, attempts were made to determine the redistribution equilibria in the system $(\text{CH}_3)_2\text{GeBr}_2$ vs. $\text{CH}_3\text{P}(\text{O})(\text{OC}_6\text{H}_5)_2$ involving exchange of Br and OC_6H_5 groups. However, no reaction was observed after heating at 150°C for 25 days and it was concluded that the equilibrium must lie completely to the side of the reactants. Table IV, System (N), shows that indeed the intersystem constant $K_{\text{I}(\text{Ge}/\text{P})}$ for the Br/ OC_6H_5 exchange between these two moieties is very large indicating that the equilibrium lies almost completely to the side of the reactants.

Having now summarized all available intersystem constants $K_{\text{I}(\text{Ge}/\text{P})}$ and $K_{\text{I}(\text{Si}/\text{P})}$ in Table IV, a correlation between these constants may be attempted. Such a correlation is facilitated when the constants of Table IV are plotted as shown in Figure 1. For the halogen-halogen exchange equilibria, the following conclusions may be drawn: (a) the equilibria in the $(\text{CH}_3)_2\text{Ge}$ systems are closer to randomness than those in the corresponding $(\text{CH}_3)_2\text{Si}$ systems, (b) for the Cl/Br exchanges a reversal of the affinity relationship of the phosphorus moiety is seen when substituting silicon for germanium; however, the "Cl-acceptor strength" in both series increases in the order $\text{CH}_3\text{P} < \text{CH}_3\text{P}(\text{S}) < \text{CH}_3\text{P}(\text{O})$, (c) assuming

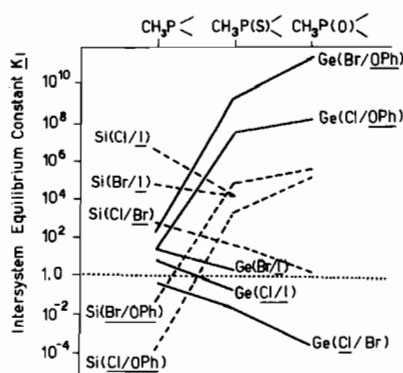


Figure 1. Plot of the intersystem equilibrium constants of Table IV. The solid lines represent the constants involving $(\text{CH}_3)_2\text{Ge}$ moieties and the broken lines represent those for the $(\text{CH}_3)_2\text{Si}$ systems. The dotted line at $K_1 = 1.0$ represents the ideal random case. The underlined substituent at equilibrium preferentially bonds to the phosphorus moiety.

parallel behavior of exchanges involving Cl/Br with those of Cl/I and Br/I, the missing intersystem constants of the latter pairs of substituents on $\text{CH}_3\text{P(O)}$ and $(\text{CH}_3)_2\text{Ge}$ may be estimated by extrapolation.

For the systems involving exchange of halogens with OC_6H_5 groups, the $(\text{CH}_3)_2\text{Ge}$ systems deviate more from randomness than the corresponding $(\text{CH}_3)_2\text{Si}$ systems.

There is no doubt such relationships, when available for a large number of systems and when properly theoretically evaluated, will contribute to our understanding of differences in the bonding properties in series such as CH_3P , $\text{CH}_3\text{P(S)}$, and $\text{CH}_3\text{P(O)}$.

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