

# REDISTRIBUTION AND EXCHANGE REACTIONS IN GROUPS IIB-VIIB

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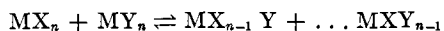
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## I. INTRODUCTION

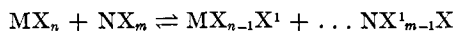
Exchange or redistribution reactions, first recognized by Calingaert (23), are very common in groups II-VII among the nontransitional elements. A great many examples of such reactions have been observed, and progress has been made toward investigating the thermodynamic and kinetic characteristics of favorable systems. Mechanistic ideas have also evolved. The scope and occurrence of these reactions are described in this review. A convenient classification of the reactions involved is:

### a. Intermolecular

- (i) where the central atom is the same and the substituents are different



- (ii) where the central atoms are different (M and N), but the substituents are the same and redistributed between M and N



- (iii) where the central atoms (M, N) and substituents (X, Y) differ



### b. Intramolecular

Involving exchange of groups between two stereochemically distinct positions in a molecule, *e.g.*, exchange of axial and equatorial fluorine in selenium tetrafluoride. (This classification takes no account of mechanism, but merely of the over-all change taking place.)

The number of possible reactions in categories a(ii) and a(iii) is very large and they are much used preparatively (36, 79), but examples of type a(i) have been studied more extensively as to thermodynamics and kinetics. Type a(i) reactions form the bulk of this review. The factors affecting all these intermolecular reactions should be similar, and it should be possible to predict reactivity for categories a(ii) and a(iii) from the trends for type a(i). The intramolecular type b is the smallest category, but as these are different in kind from the others they are fully discussed.

There has been no comprehensive review of the subject since that of Calingaert (24). Reviews from a descriptive and from a thermodynamic aspect have appeared (51, 55, 56, 71, 180, 193). Redistribution or exchange reactions are not always abstracted or indexed as such. The literature survey cannot therefore be comprehensive. The survey was made to the end of 1963, although more recent papers which have come to the author's notice have been included. Descriptive or preparative work has not usually been included unless this gave some indication of the extent and/or rate of reaction. Excluded from the review are chemical exchange methods used in the separation of isotopes, which are adequately documented elsewhere (58, 120, 182), redistribution reactions resulting in polymeric species (160, 193), and exchange between two different oxidation states of the same atom.

The notation used in this review is

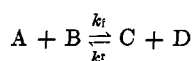
$\Delta G_r$                       Gibbs free-energy change for a redistribution reaction

$\Delta H_r$	enthalpy change
$\Delta S_r$	entropy change
$E^*$	Arrhenius energy of activation
$\Delta S^*$	entropy of activation
$J_{M^x-N^y}$	spin-spin coupling constant for spins of $M^x$ and $N^y$
$k$	rate constant
$K$	equilibrium constant

## II. EXPERIMENTAL METHODS

Experimental appraisal of a redistribution reaction depends on the rate of the particular reaction to be studied and that of its reverse reaction.

### A. LABILE SYSTEMS



$$K = \frac{[C][D]}{[A][B]} = k_f/k_r \quad (\text{Eq. 1})$$

Those reactions whose half-life is of the order of 1 min. or less at room temperature, but which have similar forward and reverse rate constants, will be referred to as labile systems ( $0.01 < K = k_f/k_r < 10^2$ ). The equilibrium is so rapidly attained that one set of products can not usually be isolated. The disproportionation is faster than the usual physical methods of separation, and maintenance of equilibrium will cause the exclusive separation of either A and B or C and D, whichever has the extreme set of appropriate physical properties (*e.g.*, the most and least volatile) (*cf.* ref. 3, 4). The presence of the products in a labile mixture such as (i) cannot be demonstrated by chemical analysis, for all intermediate compositions between A + B and C + D would be indistinguishable. Physical methods such as visible (185), Raman (44, 201), and infrared (118) spectroscopy, and nuclear magnetic resonance (40) and mass spectrum (19) measurements have been used to establish the presence of intermediate compounds in labile systems. Exchange may also be demonstrated by labeling with isotopic (141) or optically active tags (28), but the latter may be unsuitable unless configuration is retained during the exchange.

Kinetics for those labile systems have mostly been studied by nuclear magnetic resonance although, in principle, any fast reaction technique which can distinguish between reagents and products is suitable. The raw data are lifetimes of a nucleus in one environment before exchange to another. Concentration and temperature dependence of exchange lifetimes can be used to estimate rate constants and activation energies (127, 136, 187). Direct thermochemical measurements are possible. Quantitative data on equilibrium constants may be obtained from visible, Raman, and mass spectra (*vide infra*).

### B. RAPID REACTIONS PROCEEDING TO COMPLETION

Where one set of products (A + B or C + D) is 100% formed, most physical and chemical methods can be used to detect the reaction. Fast reaction techniques must be used for kinetics (187), and direct thermochemical data may be obtained.

### C. SLOW REACTIONS

For slow reactions most chemical or physical methods may be used. Heats of reaction are best obtained indirectly and ordinary kinetic techniques may be applied.

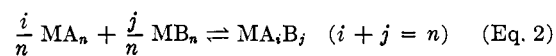
### D. INTRAMOLECULAR EXCHANGE

Detection of rapid reactions is possible by spectroscopic methods provided the exchange rate is similar in frequency to the interval between absorption frequencies of the exchanging species. Exchange lifetimes can be obtained from spectroscopic data (1, 107, 126, 136).

## III. THERMODYNAMICS

A redistribution reaction has been defined as one in which bonds change in relative position but not in total number or type (180). If one could assume constancy of bond-energy values, such reactions would be thermoneutral. Type b and type a(ii) reactions would indeed be thermoneutral as the products are identical with the reagents, but the others probably have a heat of redistribution. The free-energy change is given by the equation,  $\Delta G_r = \Delta H_r - T\Delta S_r$ . Equilibrium in a thermoneutral reaction would be governed by the  $T\Delta S_r$  term, and completely random distribution of groups would result. Distribution in reactions of type b is readily calculated statistically (24, 61, 88).

Where nonrandom distribution occurs, the equilibrium constant deviates from the statistical one ( $K \neq K_{stat}$ ), and there is a measurable enthalpy change for the reaction ( $\Delta H_r \neq 0$ ). For Eq. 2, deviation of  $K$  from the statistical value has been attributed mainly to electrostatic effects.



$$\log K_{meas} = \log K_{stat} + \log K_{e1} + \log K_r \quad (\text{Eq. 3})$$

A method of calculating electrostatic stabilization of the mixed compound for  $M = \text{Hg}$  has been described (14, 61). The over-all equilibrium constant was broken down into factors:  $K_{stat}$  favoring the mixed compound statistically;  $K_{e1}$ , to account for electrostatic stabilization; and  $K_r$ , to allow for any additional stabilization of the mixed compound. The sum of the calculated  $K_{stat}$  and  $K_{e1}$  terms in Eq. 3 reproduced the measured  $K$  term (61). Values for  $\Delta H_r$  (obtained directly from Eq. 2, or derived from heats of formation) have been taken as a measure of the difference in bond energy of MA and MB bonds in product and reactant. Approxi-

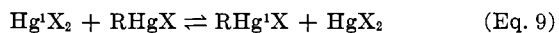
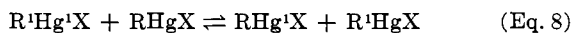
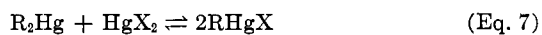
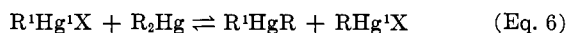
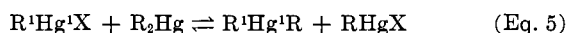
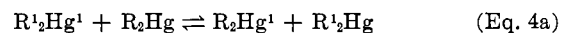
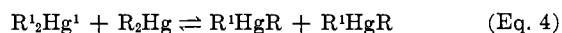
mate molecular orbital calculations of such bond-energy changes are of the same order of magnitude as the experimental data (181, 182). Entropy values  $\Delta S_r$  have also been obtained from the standard gas phase entropies of each component (calculable from spectroscopic data (103, 143, 156) if not available).

#### IV. INTERMOLECULAR REACTIONS

##### A. GROUP II

Zinc acetylacetonate (labeled with  $Zn^{65}$ ) and zinc oxinate in dioxane solution exchanged zinc completely in less than 30 sec. A heterogeneous reaction between solid oxinate and a solution of acetylacetonate was much slower (75% exchange of  $Zn^{65}$  in 12 hr.). Dissolution of the oxinate was presumed to be the rate-determining step (174). Methyl ethyl zinc could not be isolated from a mixture of dimethyl- and diethyl zinc after it had been refluxed with aluminium chloride at 60° (24). This does not necessarily imply that scrambling of alkyl groups on zinc is slow, for the system may well be labile as described in section IIA, when the mixed compound would not be isolable on distillation. Raman spectra gave evidence of mixed halocadmates,  $CdBrI_3^{2-}$ ,  $CdBr_2I_2^{2-}$ ,  $CdBr_3I^{2-}$ , in equilibrium with the halocadmates  $CdBr_4^{2-}$  and  $CdI_4^{2-}$  in aqueous solution (171). Although the large numbers of lines permitted by the selection rules for the mixed halocadmates were not resolved, the symmetrical breathing made at 117  $cm^{-1}$  ( $CdI_4^{2-}$ ) and 166  $cm^{-1}$  ( $CdBr_4^{2-}$ ) was altered in the mixtures to a broad unresolved band whose frequency depended on the ratio of bromide to iodide in the mixture. Mixed halides and halo complexes of mercury are discussed in a recent review (43).

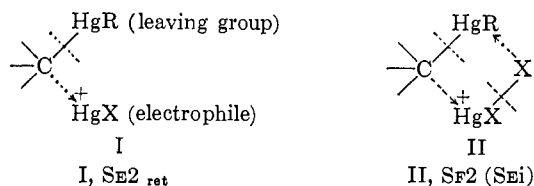
Six possible exchange reactions involving alkylmercury compounds were listed by Charman, Hughes, and Ingold (29). To these (Eq. 4-9) may be added reaction 4a. For three of these,  $SE_2$  electrophilic substitution on carbon by a mercuric species was considered a possible mechanism, and experimental tests were employed to explore this hypothesis (27-30, 101). The labels in Eq. 4-9 may not be required in practice. Reaction 6 has not yet been observed, but examples of all the others are known.



Mixtures of dimethylmercury and perdeuteriodimethylmercury after 78 hr. at 65° contained the  $CH_3$ - $HgCD_3$  species, identified by mass spectra based on the  $Hg^{200}$  isotope (52) (Eq. 4). Exchange of radioactive

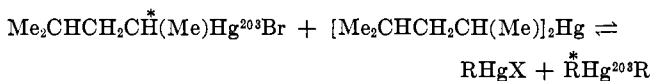
mercury between diphenylmercury and ditolylmercury appeared to be an example of Eq. 4a; no unsymmetrical diarylmercury was produced (162). Random distribution of methyl and ethyl groups on mercury was found for the catalyzed reaction of dimethyl- and diethylmercury at high temperatures (24).

Reaction 5 has been observed with *sec*-butylmercuric bromide and di(*sec*-butyl)mercury (29). The butylmercuric bromide was doubly labeled: (a) using optically active *sec*-butyl and (b) using radioactive mercury. The rate of alkyl exchange (as measured polarimetrically) was equal to the rate of mercury exchange (radiometric). Thus one alkyl group was exchanged in each mercury transfer. The possibility expressed in Eq. 6 was not observed for it would have meant no loss in radioactivity of alkylmercuric halide. Second-order kinetics and retention of configuration were consistent with two mechanisms: bimolecular electrophilic substitution at carbon with front-side attack ( $SE_{2ret}$ , structure I) and a four-center mechanism ( $SF_2$  or  $SE_i$ , structure II). The breaking of the mercury-carbon



bond and formation of the new one must occur in concert and on the same side of the optically active carbon atom to preserve configuration. The two transition states differ essentially in the importance of mercury-halogen bond breaking and making. A third type of mechanism  $SE_1$  (rate-determining fission of carbon-mercury bond to give a carbanion) is ruled out by the second-order kinetics and the stereochemical result. An increase in rate found when X was changed, paralleled the increasing ionicity of  $HgX_2$  ( $X = NO_3 > OAc > Br$ ) (see Table I). A low affinity of  $X^-$  for Hg would favor the  $SE_2$  mechanism.

Exchange of doubly labeled 1,3-dimethylbutylmercuribromide with the corresponding dialkylmercury



provided another example. Transfer of the optically active group with complete retention of configuration accompanied exchange of  $Hg^{203}$  (165).

Redistribution of a dialkylmercury and a mercuric halide to the alkylmercuric halide proceeds to completion. The heat of redistribution  $\Delta H_r$  obtained from heats of formation of the three species involved (Eq. 7) is larger for the more ionic halides ( $Cl > Br > I$ ) indicating the largest change in bond character on formation of alkylmercuric chloride (section III) (Table II) (180).

TABLE I  
 KINETIC DATA FOR REACTIONS 5 AND 9 IN ETHANOL<sup>a</sup>

HgMN'	HgNN'	Temp., °C.	$k_2$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	Added salt	Concn., M	Ref.
<i>sec</i> -BuHgBr	<i>sec</i> -Bu <sub>2</sub> Hg	35	$4.6 \times 10^{-5}$	...	...	29
<i>sec</i> -BuHgBr	<i>sec</i> -Bu <sub>2</sub> Hg	35	$5.0 \times 10^{-5}$	LiOAc	0.1	29
<i>sec</i> -BuHgBr	<i>sec</i> -Bu <sub>2</sub> Hg	35	$6.0 \times 10^{-5}$	LiNO <sub>3</sub>	0.1	29
<i>sec</i> -BuHgBr	<i>sec</i> -Bu <sub>2</sub> Hg	35	$10.0 \times 10^{-5}$	LiBr	0.1	29
<i>sec</i> -BuHgBr	<i>sec</i> -Bu <sub>2</sub> Hg	35	$12.0 \times 10^{-5}$	LiClO <sub>4</sub>	0.1	29
<i>sec</i> -BuHgOAc	<i>sec</i> -Bu <sub>2</sub> Hg	35	$2.7 \times 10^{-4}$	...	...	29
<i>sec</i> -BuHgNO <sub>2</sub>	<i>sec</i> -Bu <sub>2</sub> Hg	0	$3.4 \times 10^{-2}$	...	...	29
<i>sec</i> -BuHgNO <sub>2</sub>	<i>sec</i> -Bu <sub>2</sub> Hg	0	$4.9 \times 10^{-2}$	LiNO <sub>3</sub>	0.15	29
CH <sub>3</sub> HgBr <sup>b</sup>	HgBr <sub>2</sub> <sup>b</sup>	100.2	$1.28 \times 10^{-4}$	...	...	101
CH <sub>3</sub> HgI <sup>b</sup>	HgI <sub>2</sub> <sup>b</sup>	100.2	$10.1 \times 10^{-4}$	...	...	101
CH <sub>3</sub> HgOAc <sup>b</sup>	Hg(OAc) <sub>2</sub> <sup>b</sup>	59.8	$5.0 \times 10^{-3}$	...	...	101
CH <sub>3</sub> HgNO <sub>2</sub> <sup>b,c</sup>	Hg(NO <sub>2</sub> ) <sub>2</sub> <sup>b,c</sup>	0	$16.9 \times 10^{-4}$	...	...	101
<i>sec</i> -BuHgOAc <sup>b</sup>	Hg(OAc) <sub>2</sub> <sup>b</sup>	59.8	$3.05 \times 10^{-4}$	...	...	101
<i>sec</i> -BuHgOAc <sup>b</sup>	Hg(OAc) <sub>2</sub> <sup>b</sup>	59.8	$4.58 \times 10^{-4}$	LiNO <sub>3</sub>	0.1	101
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$0.49 \times 10^{-1}$	...	...	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$12.8 \times 10^{-5}$	LiBr	0.035	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$21.5 \times 10^{-5}$	LiBr	0.065	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$39 \times 10^{-5}$	LiBr	0.105	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$69 \times 10^{-5}$	LiBr	0.161	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$88 \times 10^{-5}$	LiBr	0.203	30
CH <sub>3</sub> HgBr <sup>d</sup>	HgBr <sub>2</sub> <sup>d</sup>	59.8	$121 \times 10^{-5}$	LiBr	0.271	30

<sup>a</sup> Reagents were 0.1 M unless otherwise stated (29–31). <sup>b</sup> Mean values for several reagent concentrations. <sup>c</sup> 0.32 M HNO<sub>3</sub>, 0.8% H<sub>2</sub>O added. <sup>d</sup> 0.095 M.

 TABLE II  
 THERMODYNAMIC DATA FOR SCRAMBLING REACTIONS<sup>a</sup>

Compound	$\Delta H_r$	Compound	$\Delta H_r$	Compound	$\Delta H_r$
BClF <sub>2</sub> <sup>b</sup>	$0.49 \pm 0.03$	PClBr <sub>2</sub> <sup>c</sup>	$0.20^e$		
BCl <sub>2</sub> F <sup>b</sup>	$0.7 \pm 0.04$	PCl <sub>2</sub> Br <sup>c</sup>	$-0.8^e$		
MeHgCl <sup>d</sup>	-6.6	EtHgCl <sup>d</sup>	-7.3		
MeHgBr <sup>d</sup>	-4.6	EtHgBr <sup>d</sup>	-5.1	Me <sub>3</sub> SnBr <sup>f</sup>	$-10.8 \pm 3.0$
MeHgI <sup>d</sup>	-3.2	EtHgI <sup>d</sup>	-2.6	Si(OEt) <sub>3</sub> Cl <sup>g</sup>	-4.3
B(OEt) <sub>2</sub> Cl <sup>f</sup>	$-4.0 \pm 0.7$	P(OEt) <sub>2</sub> Cl	-3.2	Si(OMe) <sub>3</sub> Cl	-3.82
				Si(OMe) <sub>2</sub> Cl <sub>2</sub>	-4.72
B(OEt)Cl <sub>2</sub> <sup>f</sup>	$-4.8 \pm 0.7$	P(OEt)Cl <sub>2</sub>	-3.2	Si(OMe)Cl <sub>3</sub>	-3.79
B(NMe <sub>2</sub> ) <sub>2</sub> Cl <sup>g</sup>	-8.9	P(NEt <sub>2</sub> ) <sub>2</sub> Cl	-8.6 <sup>h</sup>	Si(NMe <sub>2</sub> ) <sub>3</sub> Cl	-7.8 <sup>k</sup>
				Si(NMe <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	-9.1 <sup>k</sup>
B(NMe <sub>2</sub> )Cl <sub>2</sub> <sup>g</sup>	-12.1	P(NEt <sub>2</sub> )Cl <sub>2</sub>	-9.0 <sup>h</sup>	Si(NMe <sub>2</sub> )Cl <sub>3</sub>	-6.5 <sup>k</sup>
Si(OMe) <sub>3</sub> OEt	0.017	MeP(NEt <sub>2</sub> )Cl <sup>h</sup>	-6.4 <sup>h</sup>	Me <sub>2</sub> Si(NMe <sub>2</sub> )Cl <sup>i</sup>	-3.46 <sup>k</sup>
Si(OMe) <sub>2</sub> (OEt) <sub>2</sub>	0.010	P(OMe) <sub>2</sub> OEt	0.119	MeSi(NMe <sub>2</sub> ) <sub>2</sub> Cl <sup>i</sup>	-3.4 <sup>k</sup>
Si(OMe)(OEt) <sub>3</sub>	0.052	P(OMe)(OEt) <sub>2</sub>	0.107	MeSi(NMe <sub>2</sub> )Cl <sub>2</sub> <sup>i</sup>	-4.0 <sup>k</sup>

<sup>a</sup> In kcal. mole<sup>-1</sup>; gas phase data unless otherwise stated; data from ref. 197 except where noted. <sup>b</sup> Ref. 158. <sup>c</sup> Ref. 69. <sup>d</sup> Ref. 180. <sup>e</sup> Ref. 67. <sup>f</sup> Ref. 182. <sup>g</sup> Ref. 181. <sup>h</sup> Ref. 195. <sup>i</sup> Ref. 196. <sup>j</sup> Ref. 153. <sup>k</sup> Probably liquid phase but not stated.

TABLE III<sup>a</sup>

Reaction x		Reaction x, kcal. mole <sup>-1</sup>		Reaction y		Reaction y, kcal. mole <sup>-1</sup>	
2AsA <sub>2</sub> B ⇌ AsA <sub>3</sub> + AsAB <sub>2</sub>		$\Delta H_r$		2AsAB <sub>2</sub> ⇌ AsB <sub>3</sub> + AsA <sub>2</sub> B		$\Delta G_{diff}$	
A	B	$\Delta H_r$	$\Delta G_{diff}$	$\Delta H_r$	$\Delta G_{diff}$		
C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Cl	3.8	1.79 (252°)	2.6	1.83 (256°)		
N(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	F	2.0	5	3.6	7		
OCH <sub>3</sub> <sup>c</sup>	F	1.7	1.2	2.4	1.5		
N(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	Cl	6.8 <sup>e</sup>	5.5	6.9 <sup>e</sup>	5.5		
OCH <sub>3</sub> <sup>c</sup>	Cl	3.4	1.8	3.8	2.6		
N(CH <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	Br	7–9 <sup>e</sup>	7.7	6–7 <sup>e</sup>	7.3		
OCH <sub>3</sub> <sup>d</sup>	Br	2.2	2.0	2.2	1.9		

<sup>a</sup> Authors did not state whether data were referred to gas phase. <sup>b</sup> Ref. 63. <sup>c</sup> Ref. 133, 25°. <sup>d</sup> Ref. 133, 40°. <sup>e</sup> Best value obtained from several reactions.

The data in Table II refer to the reaction in Eq. 2.

Kinetics of reaction 7 when R is alkyl or aryl are second order in dioxane (Table IV). In a series of alkyl and aryl compounds, there are large changes in  $\Delta S^*$ , but  $E^*$  changes little. For *para* substituents in the phenyl group, a Hammett correlation between  $\log k$  (25°) and  $\sigma$  was linear with a high negative  $\rho$  (-5.87) ( $s = 0.16$  and  $r = 0.993$ ). The  $\rho$  value indicates that the phenyl carbon attached is a center for electrophilic attack. This and the increase in rate with ionicity of HgX<sub>2</sub> (X = Cl > Br > I) favor the SE2 mechanism, or attack by an ion pair. Phenyl-mercury bond fission in the transition state should require a different role for

TABLE IV  
REACTION  $R_2Hg + HgI_2 \rightleftharpoons 2RHgI$  IN DIOXANE

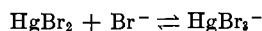
R	$k_2$ at 35°, l. mole <sup>-1</sup> sec. <sup>-1</sup>	$\Delta S^\ddagger$	$E^\ddagger$ , kcal. mole <sup>-1</sup>	Ref.
Cyclopropyl	$0.14 \times 10^{-2}$	-22	12.8	53
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	$2.96 \times 10^{-2}$	-29	12.0	53
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	$3.48 \times 10^{-2}$	-28	12.2	53
C <sub>2</sub> H <sub>5</sub>	$3.20 \times 10^{-2}$	-28	12.3	53
C <sub>6</sub> H <sub>5</sub>	3.90	-16	12.8	53
C <sub>6</sub> H <sub>5</sub> <sup>a</sup>	113.0	-13	11.7	54
C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	43.0	-28	7.6	54
C <sub>6</sub> H <sub>5</sub> <sup>c</sup>	23.2	-31	7.6	54

<sup>a</sup> Solvent ethanol. <sup>b</sup> Solvent benzene. <sup>c</sup> Solvent cyclohexane.

each phenyl attached to mercury, one as an electron donor, another as electron acceptor. The appropriate dependence of  $k$  on  $\sigma \log k/k^0 = \sigma\rho + \sigma\rho'$  apparently is not observed (54). Variation of rate with solvent was also investigated (Table IV). The same workers reported exchange of Hg<sup>203</sup> in methanol solution between Hg<sup>203</sup>Cl<sub>2</sub> and PhHgEt producing PhHgCl and EtHgCl of equal radiotracer content (54).

Other workers (145), however, claim that they are unable to repeat the work and that exchange of Ph-HgEt with radioactive mercuric chloride or bromide under a variety of conditions produced phenylmercuric halide as the only radioactive product and inactive ethylmercuric halide. The statistical occurrence of radioactivity in phenyl and ethylmercuric halides could only be explained on unusual transition states in which both mercury atoms were equivalent (54). Some additional experimentation would seem essential here.

Reaction of di-*sec*-butylmercury (with one optically active carbon per molecule) and mercuric salts was first order in each reagent and proceeded with retention of configuration (104). A higher rate of reaction for more ionic mercury salts (NO<sub>3</sub> > OAc > Br) favored an S<sub>E</sub>2 mechanism. The specific retardation of bromide ion on the mercuric bromide reaction was attributed to loss of electrophilicity on complex salt formation



as expected for an S<sub>E</sub>2 reaction (Table V) (28). Lack of an appreciable salt effect (LiI) on the diphenylmercury-mercuric iodide reaction (53) was questioned by these authors (29).

The work of the Russian school on the stereochemistry and kinetics of the two-alkyl exchange (Eq. 7) up to 1960 has been reviewed by Reutov (162). The symmetrization of RHgX (reverse of Eq. 7) is considered to be an electrophilic displacement. The second-order reaction of compound III was base-accelerated. The ester grouping (Z = CH<sub>3</sub> > C<sub>2</sub>H<sub>5</sub> > *i*-C<sub>3</sub>H<sub>7</sub> > menthyl > *t*-C<sub>4</sub>H<sub>9</sub>) and phenyl substituents (Y = Cl > Br > H > CH<sub>3</sub>) exerted a large effect on the rate (163).

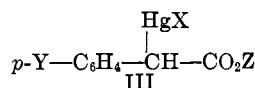


TABLE V  
SPECIAL SALT EFFECTS IN ELECTROPHILIC SUBSTITUTIONS (30)  
FOR EQUIMOLAR REAGENTS AND ADDED SALT

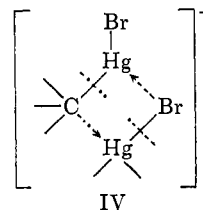
Reaction	RHgX or HgX <sub>2</sub>	Normal salt effect	Specific effect of Br <sup>-</sup> on RHgBr or HgBr <sub>2</sub> reaction
Eq. 5	Increase	2- or 3-fold increase	None
Eq. 7	Increase		Retardation
Eq. 9	Increase	2-5-fold increase	80-fold increase

A related reaction (164) (example of Eq. 8) is the exchange of radioactive mercury between phenylmercuric bromide and compound III (Y = H, Z = C<sub>2</sub>H<sub>5</sub>). In pyridine this was first order in each component and had an activation energy of 12 kcal. mole<sup>-1</sup>. Exchange in methylmercuric halides, pseudohalides, and mixtures of these, observed by n.m.r. line broadening, is also a type of reaction 8. Spin coupling ( $J_{Hg^{199}-H}$  200 c.p.s.) gives sharp satellites in the proton spectra of the cyanide, acetate, and chloride. For more highly polarizable halides, the lines are broadened by alkyl exchange. No dialkylmercury was observed (94) (Table VI).

TABLE VI  
LIFETIME OF CH<sub>3</sub>-Hg FOR CH<sub>3</sub>HgX AND FOR MIXTURES OF CH<sub>3</sub>HgX AND CH<sub>3</sub>HgY, 2.5 MOLE % IN PYRIDINE (94)

X	Lifetime, sec.	X	Y	Lifetime, sec.
I	0.01	I	SCN	0.018
SCN	0.033	I	Br	0.019
Br	0.077	SCN	Cl	0.067

Occurrence of the one-alkyl exchange (a) has been reviewed up to 1960 (101). Exchange of methyl- or optically active *sec*-butylmercuric salts with radiomercury salts was second order and preserved configuration of the carbon (101). Again the S<sub>E</sub>2 mechanism is proposed on account of the rate increase for ionic mercuric salts (Tables I and V). A very marked catalysis by ions which could coordinate with the mercuric salt (iodide on mercuric iodide, bromide on mercuric bromide) was interpreted in terms of the cyclic transition state (SE<sub>i</sub>, structure IV). This catalysis was very



marked for up to 1 mole of added ion (one-ion catalysis) and was ascribed to HgX<sub>3</sub><sup>-</sup> completing the cyclic transition state by providing an anion to combine with the leaving electrophile. For higher concentrations of added ion a further effect was noted (two-ion catalysis) which could have been due to RHgX<sub>2</sub><sup>-</sup> or HgX<sub>4</sub><sup>2-</sup>, but

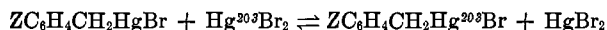
TABLE VII

Ref.	Solvent	REACTION 9 ( $R = C_6H_5-CHCO_2C_2H_5$ )		
		$k_n$ at 60°	$E^*$ , kcal. mole <sup>-1</sup>	$\Delta S^*$ , e.u.
167	Pyridine	$k_2 = 6.6 \times 10^{-2}$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	16.3	-15.5
167	Dioxane (70%)	$k_1 = 5.6 \times 10^{-4}$ sec. <sup>-1</sup>	26.7	+4.6
166	Quinoline	$k_2 = 1.1 \times 10^{-3}$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	18.8	(For $R = C_6H_5CH_2-$ )

neither species is thermodynamically favored. The decreased electrophilicity of the attacking species ( $HgX_3^-$ ) is not apparently as important as it was in reaction 7. Calculated values of rate constant, based on the hypothesis that 1 or 2 moles of anion  $X^-$  complete the transition state, reproduce the measured values closely (30).

A unimolecular  $SE1$  mechanism is postulated for reaction 9 in 70% aqueous dioxane of compound III where  $Y = H$ ,  $Z = C_2H_5$ . Exchange of  $RHgBr$  with mercuric bromide (labeled with  $Hg^{203}$ ) was first order in ester but zero order in mercuric bromide. Rate-determining C-Hg bond fission must precede rapid exchange of mercury between  $HgBr^+$  and  $HgBr_2$ . The same reaction follows the usual second-order law in pyridine (Table VII). Arrhenius parameters and rate constants are tabulated and may be compared with those in Table III. Electron-withdrawing groups in the benzene nucleus should assist ionization of the C-Hg bond. Electron donors should hinder it. The order of substituent effects is  $p-I, Br, Cl > p-F > H > o-CH_3 > p-CH_3 > p-(t-C_4H_9)$  as anticipated for the  $SE1$  mechanism (168, 170).

Other basic solvents which have been investigated are dimethylformamide (169) (in which the solvent-mercuric salt complex is the highly efficient electrophilic agent) and quinoline. Arrhenius parameters and substituent effects are given for the benzylmercuric bromide exchange with mercuric bromide in quinoline ( $Z = i-C_3H_7 > CH_3 > H > Cl > F$ ) (Table VII).



Mean lifetimes  $\tau$  of the carbon-metal bond in exchange reactions between different central atoms (type a(iii)) have been investigated using proton magnetic resonance for alkyl derivatives of group II metals (Mg, Zn, Cd, Hg) (52). Exchange was rapid except when mercury was one of the metals. Exchange of alkylmercury and other metal-alkyl systems was rather slow or nonexistent in tetrahydrofuran at 28°, dimethylmagnesium—but not zinc, cadmium, or mercury derivatives—exchanging within 8 days. Both ionic and free-radical mechanisms seem unlikely for such systems. Gas phase dissociation of group II metal alkyls to free radicals requires high temperatures. Activation energies for the dissociation.



at 465–600° were:  $M = Zn$  (47.2 kcal. mole<sup>-1</sup>),  $Cd$  (45.8 kcal. mole<sup>-1</sup>), and  $Hg$  (50.1 kcal. mole<sup>-1</sup>) (159).

Dimethylcadmium can apparently exchange methyl

TABLE VIII

LIFETIME OF CARBON-METAL BONDS				
A (M)	B (M)	Solvent	$\tau$ , sec.	Ref.
$Me_2Al$ (0.062)	$Me_2Cd$ (0.097)	Benzene	<0.09	127
$Me_2Mg$ (0.33)	$Me_2Zn$ (0.33)	Tetrahydrofuran	<0.009	52
$Me_2Mg$ (0.60)	$Me_2Cd$ (0.60)	Tetrahydrofuran	<0.007	52
$Me_2Mg$ (0.60)	$Me_2Hg$ (0.60)	Tetrahydrofuran	>0.040	52
$Me_2Hg$ (0.60)	$Me_2Zn$ (0.60)	Tetrahydrofuran	>0.058	52
$Me_2Hg$ (0.60)	$Me_2Cd$ (0.60)	Tetrahydrofuran	>0.073	52

TABLE IX

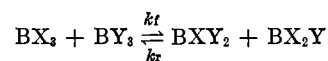
REACTION OF  $Me_2Zn$  AND  $Me_2Cd$  AT EQUAL CONCENTRATIONS

Solvent	$Me_2Cd$ concn., M	Apparent order, $n$	Apparent rate constant, $k$ , (moles/l.) <sup>1-n</sup> sec. <sup>-1</sup>
Nitrobenzene	0.492	1.6	9.1
Pyridine	0.240	2.0	12.2
Benzene	1.35	1.8	5.7
Cyclohexane	2.80	1.4	5.5

groups quite rapidly in a basic solvent. Satellites due to the  $Cd^{113}-H^1$  spin-spin coupling ( $J = 48$  c.p.s.) in the proton spectrum in hexane disappeared in the tetrahydrofuran solution spectrum. In agreement with these results (see Table VIII), previous n.m.r. studies on dimethylzinc or -cadmium mixtures with dimethylmercury exhibited no exchange phenomena (127). However, dimethylzinc-dimethylcadmium mixtures exchanged at a rate suitable for n.m.r. observation. An apparent order of 1.7 was obtained for the reaction. The difficulties of obtaining accurate rate data from careful n.m.r. work are underlined by the details in Table IX (127). Little solvent effect is apparent, excluding an ionic mechanism or a highly polar transition state.

### B. GROUP III

Redistribution reactions in boron chemistry have been discussed (11, 78, 114). Mixtures of simple boron trihalides are known to exist only in equilibrium with the corresponding mixed halides. The near-random



distribution of halogen is rapid. Lifetimes of fluorine on any boron are more than  $10^{-2}$  sec. (40) as deduced from n.m.r. data, and the slowest reaction studied ( $X = F, Y = Cl$ ) had a half-life of ca. 10 min. The rate content for this reaction ( $k_t \approx 5$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) was evaluated from change in infrared absorption intensity on a fast-scan infrared spectrophotometer (149). Beer's law does not usually hold for infrared

intensity measurements (41) and the figure is only approximate. Equilibrium constants for the chlorine-bromine and chlorine-fluorine redistributions have been calculated using Raman or infrared absorption intensity as a measure of concentration (Table X), and the same restrictions apply. The mass spectrometer gives more reliable data (Table X).  $\Delta S_r$  was calculated by statistical methods to be 4.36 e.u. for the F-Cl exchange. The heat of reaction was obtained from variation of  $K$  with temperature (91, 158) and from the relation  $\Delta G_r = \Delta H_r - T\Delta S_r$  (91). The heats of reaction from infrared and mass spectrum measurements are in reasonable agreement.

Lindemann and Wilson obtained gas phase vibration spectra for the exchange on boron of fluoride-chloride, fluoride-bromide, and chloride-bromide. Assignment of every observed frequency of the mixed halides was made in good agreement with values calculated using force constants, bond lengths, and angles derived for the pure halides. The mixed halides were thus shown to be planar molecules of  $C_{2v}$  symmetry. No dimeric species (potential intermediates) were detected (118). Thermodynamic properties of pure and mixed boron halides have been calculated from these spectroscopic data and estimated molecular parameters, using statistical procedures (91, 143).

Boron chloro- and bromoiodides have been observed by Raman spectroscopy (49), phenylboron chlorobromide by infrared and n.m.r. (66), ethylboron chlorofluoride (38) and boron chlorofluorobromide by n.m.r. (40), and vinylboron chlorofluoride, methyl- and ethylboron chlorofluorides, and methylboron bromofluoride by mass spectrometry (19). Only the halogen in these compounds is labile at ambient temperatures (19). The existence of mixed halogenoborate ions has been postulated (108). A rapid exchange of halogen certainly occurs between tetrahaloborates. Accurate rate and equilibrium data for these reactions are still lacking.

Mixed boron esters readily change to the symmetrical esters. Rapid exchange of ester groupings has been found for isobutylborinic and isobutylboronic esters. The methyl borinate and diethyl boronate (*i*-Bu<sub>2</sub>BO-CH<sub>3</sub> and *i*-BuB(OEt)<sub>2</sub>) equilibrated to give a mixture containing all the possible components. The O-CH<sub>3</sub> singlet hydrogen resonances were used for a quantitative n.m.r. analysis of the system. Lifetime of the methoxy groups before exchange was between 0.32 and 1.8 sec. (130) at room temperature. Attempts to isolate mixed esters of boron have failed except for cyclic compounds (65) and certain *o*-nitrophenoxy esters (35) which have some feature stabilizing the mixed compound.

Koster has discussed isomerization and catalysis in alkylboron exchange (111), and Gerrard has reviewed redistribution in systems containing boron-alkyl linkages (78). Lower boron alkyls (CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) change

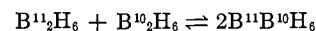
TABLE X

$K = \frac{[BXY_2][BX_2Y]}{[BX_3][BY_3]}$						
X	Y	K	Temp., °C.	Method used to obtain K	$\Delta H$ , kcal. mole <sup>-1</sup>	Ref.
F	Cl	0.53	27-29	Infrared	1.68 <sup>a</sup>	91, 98
F	Cl	0.48	15	Infrared	1.1 <sup>b</sup>	91
F	Cl	0.58	40	Infrared		91
F	Cl	1.6	27	Mass spectrometry	1.19 ± 0.07 <sup>b</sup>	158
Br	Cl	6.8		Raman		85
Br	Cl	9		Raman		57

<sup>a</sup> From  $\Delta G = \Delta H - T\Delta S$ . <sup>b</sup> From  $\Delta G = RT \ln K$ .

to symmetrical compounds rapidly at and below room temperatures, but mixed boron alkyls containing heavier alkyl groups (*e.g.*, butyl) have been prepared (112, 131, 152). This surprising result has not been satisfactorily accounted for. Replacement of a simple alkyl group by vinyl gives stable mixed compounds such as vinyl dimethylboron (83).

Exchange between diborane(6) and perdeuteriodiborane(6) in the gas phase at 24-44° is of 3/2 order and has an activation energy of 21.8 ± 3 kcal. mole<sup>-1</sup> (124). Rate-determining attack of a BH<sub>3</sub> fragment on deuteriodiborane or of BD<sub>3</sub> on diborane is consistent with the data although there have been differences of opinion about the mechanism (76). The exchange between diborane containing the B<sup>11</sup> isotope and diborane containing the B<sup>10</sup> isotope was stated to have a similar rate at 25° (179). Exchange in boron hydrides is frequently con-



nected with aggregation to higher boron hydrides. The topic has been extensively treated (110, 119). Intramolecular exchange is discussed in a later section (199, 200).

Reaction of boron halides with boron esters is an excellent preparative method for many alkoxyboron halides (78). Diethoxyboron chloride is 4.0 ± 0.7 kcal. mole<sup>-1</sup> and ethoxyboron dichloride is 4.8 ± 0.7 kcal. mole<sup>-1</sup> more stable than the appropriate mixture of boron halide and boron ester from which it is formed. Reaction to form the alkylaminoboron chlorides is even more exothermic, bisdiethylaminoboron chloride and diethylaminoboron dichloride being stabilized by 8.9 and 12.1 kcal. mole<sup>-1</sup>, respectively (Table II). If it is assumed that the order of back coordination to boron in these compounds is N > O > Cl, molecular orbital methods can be used to verify the magnitude of these stabilities (182). Dimerization of the dichloro product *via* the nitrogen is a complicating feature of these reactions (10, 84, 92).

Trialkylboranes react with boron trihalides at high temperatures giving alkylhaloboranes. The relative stability to disproportionation of the mono- and dialkylhaloboranes is inverted from chloride to bromide. Dialkylbromoboranes and alkyl dichloroboranes are stable, but alkyl dibromo- and dialkyl chloroboranes are unstable to disproportionation (128, 129). It seems

TABLE XI

Ref.	Reaction	K (gas phase, 25°)	$\Delta G$ , kcal. mole <sup>-1</sup> (25°)
177	$6(\text{CH}_3\text{O})_2\text{BH}(\text{g}) \rightleftharpoons \text{B}_2\text{H}_6(\text{g}) + 4\text{B}(\text{OCH}_3)_3(\text{g})$	$63 \pm 5$	-0.41
172	$\begin{array}{c} \text{CH}_2\text{O} \\   \\ \text{C} \\   \\ \text{CH}_2\text{O} \end{array} \text{BH}(\text{g}) \rightleftharpoons \frac{1}{3}\text{B}_2\text{H}_6(\text{g}) + \begin{array}{c} \text{CH}_2\text{O} \\   \\ \text{C} \\   \\ \text{CH}_2\text{O} \end{array} \text{BOCH}_2\text{CH}_2\text{OB} \begin{array}{c} \text{OCH}_3 \\   \\ \text{C} \\   \\ \text{OCH}_3 \end{array}$	$0.38 \pm 0.007^a$	$0.6 \pm 0.1$
184	$2\text{C}_2\text{H}_5\text{B}_2\text{H}_5(\text{g}) \rightleftharpoons \text{B}_2\text{H}_6(\text{g}) + \text{sym}-(\text{C}_2\text{H}_5)_2\text{B}_2\text{H}_4(\text{g})$	$0.039 \pm 0.006^b$	

<sup>a</sup> Heterogeneous reaction,  $K = 25$ . <sup>b</sup> Liquid phase,  $K = 0.169$ .

unlikely that the explanation for these striking differences between similar compounds is mechanistic. Both kinetic and thermodynamic studies of these systems should be rewarding.

Scrambling of halogen and hydrogen occurs in borane-boron halide mixtures, a fact utilized in the classic Schlesinger and Burg preparation of diborane (176). Difluoroborane, which could be isolated from the boron trifluoride-diborane reaction, slowly regenerated them



at room temperature (39). Curiously this species appears to be monomeric as does the chloro analog. Dichloroborane may not disproportionate so readily at room temperature as has been thought (109, 121). It has been stabilized as the etherate or in the presence of its disproportionation products (142, 150).

Alkoxyboranes are isolable. Disproportionation equilibria are given in Table XI. As in Table XI, the cyclic 1:3 dioxaborolane is only stabilized by about 1 kcal./mole<sup>-1</sup> in comparison to the acyclic dimethoxyborane (172, 177). Kinetics of the decomposition of gaseous dimethoxyborane show the reaction to be heterogeneous with an activation energy of 14.2 kcal. mole<sup>-1</sup> and a rate constant (60°)  $k = 1.69 \times 10^{-6}$  mole<sup>-1</sup> min.<sup>-1</sup>. A dimeric four-center transition state, stabilized by the surface of the vessel, was proposed (191). An essential intermediate in this mechanism, the monomethoxyborane  $(\text{CH}_3\text{O})\text{BH}_2$ , has never been isolated or even detected as such, but a polymer (21) of the correct composition has been reported (191) and it does catalyze the decomposition.

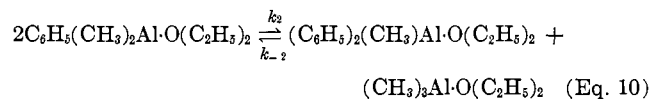
Alkyl-hydrogen exchange on boranes also occurs (177). Some alkylated boranes disproportionate very readily, e.g., ethylborane which disproportionates to *sym*-diethylborane and diborane inside 5 min. The nature of the *sym*-diethylborane formed (*cis* or *trans*) is unknown (115). Table XI contains equilibrium data for the reaction.

Redistribution of halogen on aluminium halides occurs but no extensive investigation has been made (37, 198). Aluminium halides, alkyls, and hydrides have been found to undergo or to catalyze (probably by rapid re-

TABLE XII

Species	$\beta_{ij}$	Species	$\beta_{ij}$
$\text{InCl}_2^+$	316.2	$\text{TlBrCl}^-$	6.3
$\text{InBrCl}^+$	346.7	$\text{TlBr}_2\text{Cl}^-$	8.45
$\text{InBr}_2^+$	33.1	$\text{TlBrI}^-$	172
$\text{InCl}_3$	3548.0	$\text{TlI}_2\text{Br}^-$	260
$\text{InCl}_2\text{Br}$	724.4		
$\text{InBrCl}_3^-$	794.3		

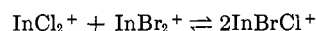
distribution) a great many scrambling reactions (24, 99, 100, 173). The tremendous importance of aluminum alkyls in the preparation of Ziegler catalysts has been much discussed (12, 202). For the many dimeric alkyls, dissociation and formation of bridged transition states provide a reasonable mechanism (183). Formation of a mixed methylisopropylalane from the dimeric methylalane and the monomeric isopropylalane was neatly demonstrated by the dimeric nature of the product (157). Proton magnetic resonance has also established the occurrence of rapid exchange reactions in alkyl and arylalanes (134, 189). Intramolecular exchange is discussed in a later section. The presence of ether as a solvent slowed down the scrambling of



phenyl and methyl groups on aluminum, presumably necessitating a dissociation step in Eq. 10 prior to the proposed four-center transition state (134). The equilibrium constant for Eq. 10 was approximately 8. The meager thermodynamic and kinetic information available does not reflect the widespread occurrence and importance of redistribution reactions in the chemistry of aluminum (202). Gallium likewise has been little studied from this viewpoint and there is scope for much research here.

Formation constants  $\beta_{ij} = [\text{MX}_i\text{Y}_j]/[\text{M}][\text{X}]^i[\text{Y}]^j$  for the complex halogeno ions of indium and thallium have been measured in solution containing metal, bromide, chloride, and iodide ions. Mixed halogeno ions were found for monovalent thallium and trivalent indium. Polarographic and potentiometric determinations were used for the indium complexes, solubility values for the thallium complexes (73).

From the formation constants in Table XII, the equilibrium constant for the reaction



is calculated to be 11.49, favoring the mixed compound. As implied by the stepwise formation constants, exchange of halogen in these systems can occur by dissociation or hydrolysis of one halogeno group followed by attachment of another.

Proton magnetic resonance spectra of trimethyl-thallium (a monomer) show pronounced  $\text{Tl}^{203}$  or  $^{205} - \text{H}^1$  spin coupling ( $J = 250.4$  c.p.s.) at low temperatures.



Collapse of the spin-spin splitting at room temperature implied intermolecular exchange of methyl groups. The activation energy in toluene- $\alpha, \alpha$ - $t_2$  was  $6.3 \pm 0.5$  kcal. mole $^{-1}$  and the reaction order was 1.84. The lifetime  $\tau$  of methyl groups before exchange was somewhat greater in the coordinating solvents trimethylamine and dimethyl ether. Formation of the postulated dimeric SF<sub>2</sub> transition state would be hindered for the complexed trimethylthallium (see Table XIII). A mixed vinyl-

TABLE XIII

LIFETIMES OF CH<sub>3</sub>-Tl BONDS AT 26° (122)

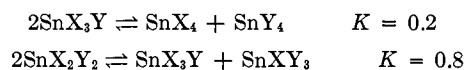
Solvent	[Tl(CH <sub>3</sub> ) <sub>3</sub> ], <i>M</i>	$\tau \times 10^{-3}$ sec.
Deuteriobenzene	1.22	0.54
Dimethyl ether	1.65	3.25
Trimethylamine	0.74	3.86

methylthallium exchanged groups rapidly in deuteriobenzene at 26° but both mono- and divinyl species were characterized in trimethylamine or dimethyl ether solution in which exchange was slower (122). The vinyl group in vinylalkylboranes slowed exchange relative to alkylboranes (83), but in benzene, a 1.0 *M* solution of methylvinylthallium exchanged about thirty times faster than a 1.0 *M* solution of trimethylthallium. The carbon-thallium bond in triphenylthallium was also rapidly breaking and reforming, with a lifetime of  $< 3 \times 10^{-4}$  sec. in methylene chloride and  $> 0.05$  sec. in trimethylamine. From hydrolysis of a mixture of trimethyl- and triethylthallium, three cations were obtained: dimethyl-, (CH<sub>3</sub>)<sub>2</sub>Tl<sup>+</sup>, diethyl-, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Tl<sup>+</sup>, and methylethylthallium, (CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Tl<sup>+</sup> (123). The alkyl groups on these cations exchanged much more slowly, if at all, at room temperature than in trialkylthallium. Despite the electrophilic nature of these species, the aggregation of positive charge in a SE<sub>2</sub> or SF<sub>2</sub> transition state must require too high an activation energy for rapid reaction at room temperature.

## C. GROUP IV

Some discussion of redistribution reactions in group IV has been made (59, 60). Halogens redistribute on all group IV tetrahalides. The rate of such reactions increases from silicon (reaction on heating) (45, 70, 71) through germanium (slow reaction at room temperature) (47) to tin (lifetime of halogen-tin bonds  $10^{-2} < \tau < 10$  sec.) (22). Random distribution was observed for silicon halides. Concentrations, determined directly by fractionating the reaction mixture, were within 2% (71). Raman (47) and Sn<sup>119</sup> n.m.r. (22) data were not usually sufficiently accurate to use for calculation of equilibrium constants, but one quantitative study of the Raman spectra of tin tetrachloride-tin tetrabromide mixtures has been made (50). For ratios of chloride to bromide of 13:1 and 1:13, equilibrium concentrations of mixed and end halides were

determined within 5-10% accuracy. From these details the following equilibrium constants can be calculated for the liquid phase reaction at room temperature.



These data are for X = Cl, Y = Br and X = Br, Y = Cl.

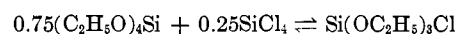
The mixed Pb<sup>11</sup> dihalides, lead chlorofluoride and lead bromochloride, were the stable entities precipitated from aqueous solutions of the appropriate ions. They are probably lattice compounds and the bromochloride was not stable in the molten state (25, 147, 148). The true equilibrium between these halides has still to be determined.



Ester group interchange on silicon, studied by gas chromatography, was almost random (197). Equilibrium concentrations for tetramethyl and tetraethyl silicate mixtures were determined to within 1% of the silicon present. Equilibrium constants (presumably for the gas phase reaction under pressure) are collected in Table XIV.

Alkyl derivatives of group IV were used in the first explicit recognition of redistribution reactions (23). The work has been reviewed (24). Kinetics for the catalyzed disproportionation of ethyltrimethylsilane indicated that the reaction was first order in catalyst (aluminum bromide), but three-halves order in silane; *i.e.*, rate =  $k[\text{Al}_2\text{Br}_6][(\text{C}_2\text{H}_5)(\text{CH}_3)_3\text{Si}]^{3/2}$ . The enthalpy of activation was 14.0 kcal. mole $^{-1}$  (neat liquid) or 9.5 kcal. mole $^{-1}$  (in benzene), and the respective entropies of activation were -45.0 and -48.6 e.u. (173). An SF<sub>2</sub> mechanism was supported by the very low entropy, the order of catalytic reactivity and substituent effects for the RSi(CH<sub>3</sub>)<sub>3</sub> disproportionation being R = H > C<sub>6</sub>H<sub>5</sub> > C<sub>2</sub>H<sub>5</sub>.

The heat of the gaseous reaction between ethyl silicate and silicon tetrachloride as derived from hydrolysis



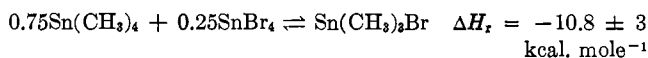
data was -4.3 kcal. mole $^{-1}$  (67). No attempt was made to extend the data to hydrolysis of other ethoxychlorosilanes because of the uncertain composition of the hydrated silica produced. Another approach has provided thermodynamic data for the methoxychlorosilanes. For the reaction of methyl silicate and silicon tetrachloride, n.m.r. analysis (accurate to about 2.3% of the total silicon present) gave equilibrium constants for dissociation of all three mixed species (Table XIV). The difference between the free energy  $\Delta G_r$  calculated from the measured equilibrium constant ( $K_{\text{meas}}$ ) and that for the statistically computed equilibrium constant ( $K_{\text{stat}}$ ) was held to be very largely an enthalpy effect, *i.e.*

$$\Delta G_{\text{diff}} = \Delta G_r - \Delta G_{\text{stat}} = (RT/n) \ln K_{\text{meas}}/K_{\text{stat}} \approx \Delta H_r$$

The values of  $\Delta H_r$  obtained by this approximation from the data in Table XIV are compared in Table II with  $\Delta H_r$  values for related reactions. The accuracy of this assumption can be gauged from the data in Table III in which  $\Delta H_r$  and  $\Delta G_{\text{diff}}$  values are compared for some arsenic reactions. Discussion of this point is made in section IVD under arsenic. When tetrakisdimethylaminosilane and silicon tetrachloride reacted, the mixed compounds were more stable by 6–9 kcal. mole<sup>-1</sup>. The same methods and treatment of data were applied (Tables II and XIV) (197). Equilibrium constants for scrambling on silicon (Si≡), methylsilicon (CH<sub>3</sub>-Si≡), and dimethylsilicon ((CH<sub>3</sub>)<sub>2</sub>Si=) entities were of similar magnitude for exchange of a particular pair of groups, e.g., OCH<sub>3</sub>-Cl. Conditions were such that

alkyl-silicon bonds were not cleaved.  $\Delta H_r$  values (calculated only for the alkylamino-chloro exchange) were always lower for the alkylsilicon compounds. Data are collected in Tables II and XIV. No quantitative study of the kinetics of these reactions has been made, but information on the time required to reach equilibrium is collected in Table XV (cf. 175).

Heats of reaction of bromine with hexamethyldistannane or tetramethylstannane were used in derivation of  $\Delta H_r$  for the gaseous reaction



This value implies considerable strengthening of bonds in trimethylbromostannane relative to tetramethylstannane and tin tetrabromide (153). The reaction of alkyl- and arylstannanes with tin halides has been

TABLE XIV

Scrambling reactions on silicon	Temp., °C.	K	Standard error	Ref.
2Si(OCH <sub>3</sub> )(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ⇌ Si(OCH <sub>3</sub> ) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	150	0.417	0.026	197
2Si(OCH <sub>3</sub> ) <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> ⇌ Si(OCH <sub>3</sub> ) <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> ) + Si(OCH <sub>3</sub> )(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	150	0.422	0.025	197
2Si(OCH <sub>3</sub> ) <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> ) ⇌ Si(OCH <sub>3</sub> ) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + Si(OCH <sub>3</sub> ) <sub>4</sub>	150	0.386	0.025	197
2CH <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (OCH <sub>3</sub> ) ⇌ CH <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + CH <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> )(OCH <sub>3</sub> ) <sub>2</sub>	120 or 150	0.26	0.01	196
2CH <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> )(OCH <sub>3</sub> ) <sub>2</sub> ⇌ CH <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (OCH <sub>3</sub> ) + CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	120 or 150	0.32	0.01	196
2(CH <sub>3</sub> ) <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> )(OCH <sub>3</sub> ) ⇌ (CH <sub>3</sub> ) <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + (CH <sub>3</sub> ) <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>2</sub>	120 or 150	0.28	0.03	196
2Si(OCH <sub>3</sub> )Cl <sub>3</sub> ⇌ Si(OCH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> + SiCl <sub>4</sub>	120	0.094	0.019	197
2Si(OCH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ⇌ Si(OCH <sub>3</sub> ) <sub>3</sub> Cl + Si(OCH <sub>3</sub> )Cl <sub>3</sub>	120	0.042	0.006	197
2Si(OCH <sub>3</sub> ) <sub>3</sub> Cl ⇌ Si(OCH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> + Si(OCH <sub>3</sub> ) <sub>4</sub>	120	0.0089	0.003	197
2CH <sub>3</sub> SiCl <sub>2</sub> (OCH <sub>3</sub> ) ⇌ CH <sub>3</sub> SiCl <sub>3</sub> + CH <sub>3</sub> SiCl(OCH <sub>3</sub> ) <sub>2</sub>	150	0.042	0.002	196
2CH <sub>3</sub> SiCl(OCH <sub>3</sub> ) <sub>2</sub> ⇌ CH <sub>3</sub> SiCl <sub>2</sub> (OCH <sub>3</sub> ) + CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	150	0.018	0.001	196
2(CH <sub>3</sub> ) <sub>2</sub> SiCl(OCH <sub>3</sub> ) ⇌ (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> + (CH <sub>3</sub> ) <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>2</sub>	120	0.010	0.002	196
2Si[N(CH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ⇌ Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> + SiCl <sub>4</sub>	25	6 × 10 <sup>-4</sup>	2 × 10 <sup>-4</sup>	197
2Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> ⇌ Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> Cl + Si[N(CH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub>	25	5 × 10 <sup>-4</sup>	6 × 10 <sup>-4</sup>	197
2Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> Cl ⇌ Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> + Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>	25	6 × 10 <sup>-6</sup>	3 × 10 <sup>-4</sup>	197
2CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> ⇌ CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl + CH <sub>3</sub> SiCl <sub>3</sub>	25	5 × 10 <sup>-4</sup>	7 × 10 <sup>-4</sup>	196
2CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl ⇌ CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> + CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	25	5 × 10 <sup>-4</sup>	6 × 10 <sup>-4</sup>	196
2(CH <sub>3</sub> ) <sub>2</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ]Cl ⇌ (CH <sub>3</sub> ) <sub>2</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> + (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	25	1.5 × 10 <sup>-4</sup>	1.6 × 10 <sup>-4</sup>	196
2CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>2</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] ⇌ CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub> + CH <sub>2</sub> Si(OCH <sub>3</sub> )[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	120 or 150	0.30	0.04	196
2CH <sub>3</sub> Si(OCH <sub>3</sub> )[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ⇌ CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>2</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> + CH <sub>3</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	120 or 150	0.40	0.05	196
2(CH <sub>3</sub> ) <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>2</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] ⇌ (CH <sub>3</sub> ) <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub> + [(CH <sub>3</sub> ) <sub>2</sub> Si[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ]	120 or 150	0.22	0.06	196

TABLE XV

TIME FOR ATTAINMENT OF EQUILIBRIUM IN SCRAMBLING REACTIONS ON SILICON (Eq. 2)				
M	A	B	Temp., °C.	Time <sup>c</sup>
Si	OCH <sub>3</sub>	Cl	120	<25 hr.
	N(CH <sub>3</sub> ) <sub>2</sub>	Cl	38	<i>t</i> <sub>1/2</sub> ≤ 400 min.
	OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	150	<4 days
CH <sub>3</sub> Si	OCH <sub>3</sub>	Cl	150	<12 hr.
	N(CH <sub>3</sub> ) <sub>2</sub>	Cl	25	<3 hr.
	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	120	40 hr. <sup>a</sup>
	OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	150	<7 days
	Cl	Br	85	>>43 hr. <sup>b</sup>
(CH <sub>3</sub> ) <sub>2</sub> Si	OCH <sub>3</sub>	Cl	120	<8 hr.
	N(CH <sub>3</sub> ) <sub>2</sub>	Cl	25	<3 min.
	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	120	40 hr. <sup>a</sup>
	OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	150	<7 days

<sup>a</sup> Catalyst, 1% Al<sub>2</sub>Cl<sub>6</sub>. <sup>b</sup> Ref. 64; refers to reverse reaction. Values from ref. 196 and 197.

much used preparatively (34). Scrambling of halogen in dibutyltin dihalides has been discussed (2).

## D. GROUP V

Although mixed chlorofluorides of nitrogen (154, 188) and mixed chlorobromo complex ions of bismuth (146) are known, the equilibria between mixed and end compounds have not been investigated. For phosphorus

$$\text{NF}_2\text{Cl} + \text{NFCl}_2 \rightleftharpoons \text{NF}_3 + \text{NCl}_3$$

and arsenic halides, the equilibria of Eq. 2 have been observed. Thermodynamic and kinetic data have been amassed. The formation of many of the mixed halides of this group has been mentioned in two recent articles (77, 151).

Mixed phosphorus, phosphoryl, and thiophosphoryl halides containing fluorine are isolable (15–18). Chloro-

TABLE XVI

REORGANIZATION OF F, Cl, Br, OC<sub>6</sub>H<sub>5</sub>, =O, =S, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, SCH<sub>3</sub>, AND SC<sub>4</sub>H<sub>9</sub> SUBSTITUENTS DIRECTLY ATTACHED TO P<sup>III</sup>, OP<sup>V</sup>, SP<sup>V</sup>, AND OP<sup>VH</sup>

Part A								
M	A	B	K <sub>1</sub> <sup>a</sup>	K <sub>2</sub> <sup>b</sup>	Temp., °C.	Time required	Ref.	
P	Cl	Br	0.2	0.7	25	<15 min.	69	
P=O	Cl	Br	0.406 ± 0.013	0.341 ± 0.012	130	<1 week	89	
			0.402 <sup>c</sup>	0.308 <sup>c</sup>	230	Hours	89	
P=S	Cl	Br	0.297 ± 0.012	0.419 ± 0.019	130	<1 week	88	
			.290 <sup>c</sup>	.383 <sup>c</sup>	230	Hours	89	
P	Cl	OC <sub>6</sub> H <sub>5</sub>	.13	.13	180	12 hr.	69	
P	Br	OC <sub>6</sub> H <sub>5</sub>	.38	.12	180	12 hr.	69	
P	OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	.394 ± 0.019	.367 ± 0.02	120	10-15 hr.	132	
P=O	OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	.224	.348	200	<7 days	132	
P	SCH <sub>3</sub>	SC <sub>4</sub> H <sub>9</sub>	.335 ± 0.005	.322 ± 0.004	120 <sup>d</sup>	<3 days	132	
P	Cl	SC <sub>4</sub> H <sub>9</sub>	.157 ± 0.05	.302	120	<2 days	132	
P	Cl	OC <sub>2</sub> H <sub>5</sub>	.0015	.0014				
P	OC <sub>6</sub> H <sub>5</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	.0015	.0016				

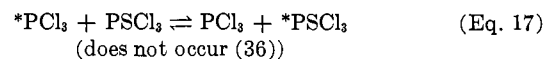
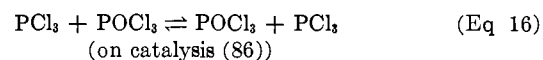
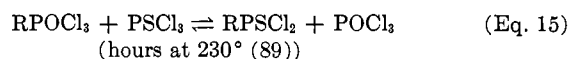
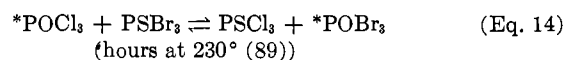
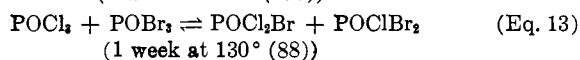
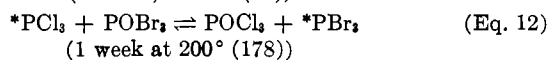
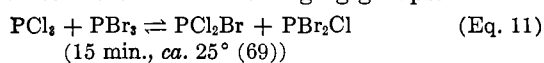
Part B

Rate	K	Temp., °C.	Time required	Ref.
[PBr <sub>2</sub> Cl][OPBrCl <sub>2</sub> ]/[PBrCl <sub>2</sub> ][OPBr <sub>2</sub> Cl]	5	200	1 week	178
[PCl <sub>2</sub> BrOC <sub>6</sub> H <sub>5</sub> ] <sup>2</sup> /[PCl <sub>3</sub> ][PBr <sub>3</sub> ][P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ]	1500	180	140 hr.	69
[PFClBr] <sup>2</sup> /[PFCl <sub>2</sub> ][PFBBr <sub>2</sub> ]	3.7	Ambient	4 hr.	48
[POCl <sub>3</sub> ][CH <sub>3</sub> PSCl <sub>2</sub> ]/[CH <sub>3</sub> POCl <sub>2</sub> ][PSCl <sub>3</sub> ]	1.4, 1.2	230	Hours	89
[POCl <sub>3</sub> ][C <sub>6</sub> H <sub>5</sub> PSCl <sub>2</sub> ]/[PSCl <sub>3</sub> ][C <sub>6</sub> H <sub>5</sub> POCl <sub>2</sub> ]	1.8, 1.7	230	Hours	89
[POCl <sub>3</sub> ][CH <sub>2</sub> ClPSCl <sub>2</sub> ]/[CH <sub>2</sub> ClPOCl <sub>2</sub> ][PSCl <sub>3</sub> ] (Eq. 15)	3.6	230	Hours	89
[POCl <sub>3</sub> ][PSCl <sub>2</sub> Br]/[POCl <sub>2</sub> Br][PSCl <sub>3</sub> ]	2.2	230	Hours	89
[POCl <sub>2</sub> Br][PSClBr <sub>2</sub> ]/[POClBr <sub>2</sub> ][PSCl <sub>2</sub> Br]	1.6	230	Hours	89
[POClBr <sub>2</sub> ][PSBr <sub>3</sub> ]/[PSClBr <sub>2</sub> ][POBr <sub>3</sub> ]	2.0	230	Hours	89
[POCl <sub>3</sub> ][PSClBr <sub>2</sub> ]/[PSCl <sub>3</sub> ][POClBr <sub>2</sub> ]	3.4	230	Hours	89
[POCl <sub>2</sub> Br][PSBr <sub>3</sub> ] <sup>2</sup> /[PSCl <sub>2</sub> Br][POBr <sub>3</sub> ]	3.1	230	Hours	89
[POCl <sub>3</sub> ][PSBr <sub>3</sub> ]/[PSCl <sub>3</sub> ][POBr <sub>3</sub> ]	6.7	230	Hours	89
[HPO(OCH <sub>3</sub> ) <sub>2</sub> ][HPO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]/[HOP(OCH <sub>3</sub> )(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>2</sup>	0.286 ± 0.024	150	<12 hr.	132

<sup>a</sup> K<sub>1</sub> = [MAB<sub>2</sub>][MA<sub>3</sub>]/[MA<sub>2</sub>B]<sup>2</sup>. <sup>b</sup> K<sub>2</sub> = [MB<sub>3</sub>][MA<sub>2</sub>B]/[MAB<sub>2</sub>]<sup>2</sup>. <sup>c</sup> Value obtained from a more complex mixture and hence less accurate. <sup>d</sup> Catalyzed by a trace of HCl.

bromides have not been isolated but have been identified by n.m.r. spectra (69) and by the Raman effect (72). Phosphorus iodobromides have been detected only by their Raman spectrum in mixtures of phosphorus tribromide and triiodide (47). Some equilibrium constants for mixed halides measured from P<sup>31</sup> n.m.r. and in one case Raman data are listed in Table XVI. The halogen exchange is close to random for all the exchanges in Table XVII, but the mixed halides are usually more stable than expected. Only the phosphorus chlorodibromide is less stable than expected. The deviation in free energy  $\Delta G_{diff}$  for each exchange is less than 1 kcal. mole<sup>-1</sup>.

In mixtures of phosphorus, phosphoryl, and thiophosphoryl halides, there are several possible exchange processes, some of which occur rapidly and others slowly at high temperatures, or only upon irradiation. Some of the processes are listed in Eq. 11-17. The isotopic labels serve to indicate the exchanging groups.



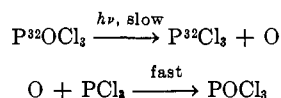
Halogen exchanges as in Eq. 11-13 occur more readily in trivalent phosphorus compounds than in the phosphoryl species. The exchange of oxygen and sulfur between two four-coordinate phosphorus species as in Eq. 15 occurred under somewhat more drastic conditions. Labeling of phosphorus was by C-P bonds (R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, or CH<sub>2</sub>Cl) which were found not to exchange under the conditions used. The most stable phosphoryl halide in this reaction and reaction 14 had the largest number of chlorine attached to it, and the most favored thiophosphoryl halide had the least. Values of equilibrium constants in Table XVII bringing out this point have been interpreted in terms of electronegativity of groups attached to phosphorus (89). Equations 16 and 17 represent a change of oxidation state of phosphorus from three to five, i.e., ex-

change of oxygen between two phosphorus atoms. The radioactive isotope  $P^{32}$  was used in a study of this reaction, which was only observed after catalysis (86). Less than 2% exchange had occurred after 23 days at  $250^\circ$  (compare Eq. 12 and 15), but a trace of moisture allowed 70% completion in less than 12 days. The exchange took place at  $25$  or  $50^\circ$  when catalyzed by ultraviolet or  $\gamma$ -irradiation. The rate of  $P^{32}$  exchange was first order in radiation dosage, first order in phosphoryl chloride, but less than first order in phosphorus trichloride. The amount of phosphorus exchange  $M$  was best expressed by

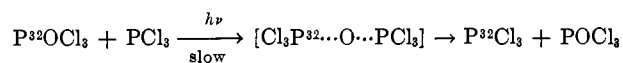
$$M = [POCl_3] + c[POCl_3][PCl_3]$$

where  $c$  is a constant involving the radiation.

Two competing mechanisms, one first order in phosphoryl chloride only, and the other first order in both reagents, were postulated to explain the rate dependence (86).



and



If this unimolecular process occurs in reaction 16, it is unlikely to be a mechanism for the much more rapid, uncatalyzed exchanges of Eq. 12–15. Ionization mechanisms involving halogen, or a four-center transition state, are more likely. The four-center transition state is not reasonable in reaction 16, as only one group has to be transferred.

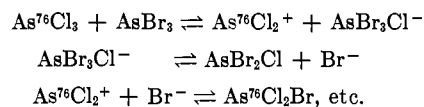
Substituent distribution very close to random was exhibited in mixtures of two trialkyl phosphites, two trialkyl phosphates, two trialkyl thiophosphites, or two dialkyl hydrogen phosphites (132). Equilibrium data, obtained from quantitative n.m.r. work, are given in Table XVI. Again a pronounced rate difference was observed between  $P^{III}$  and  $P^V$  compounds as indicated by the time and temperature required for reaction quoted in Tables XVI. Whereas the trialkyl phosphites (but not the triaryl) rearranged in 15 hr. at  $120^\circ$ , 7 days and higher temperature were required for the corresponding phosphates. Thioesters exchanged more slowly than oxyesters, even when catalyzed. Catalysts caused considerable rate increases. For trialkyl and dialkyl phosphites and phosphates, acid increased the rate. Base catalysis occurred for the trialkyl phosphates but not, strangely, for the dialkyl hydrogen phosphites which are also four-coordinate compounds.

Exchange of phenoxy and halogen groups on trivalent phosphorus gave more than the random amount of mixed compound except in formation of the dibromo compound. For ethoxy and chloro exchange the equilibrium lay almost completely in favor of the mixed

compound (68) (see Table XVI). Alkylamino and chloro groups afforded extremely stable mixed  $P^{III}$  compounds. Equilibrium was so far in their favor that accurate equilibrium constants ( $10^{-7}$  or less) could not be determined except from enthalpy data. The heat of the very rapid reaction (at  $25^\circ$ ) was measured for liquid mixtures, and, by equating  $\Delta H_r$  to  $\Delta G_{diff}$ , a value was deduced for  $K$ . Enthalpy data were quoted in Table II (195). Alkylamino-bromo exchange on  $P^{III}$  was similarly rapid and exothermic at  $25^\circ$ .

Competitive reactions occurred as well as redistribution in certain phosphorus systems. Arbuzov rearrangements of tributyl phosphites after several days at  $200^\circ$  prevented examination of redistribution involving them (132). A mixture of trialkyl phosphites and thiophosphites gave a sludge on heating, but no exchange was detected, even under catalysis (132). When phosphoric acid was one of the reagents, condensation reactions were also possible (194). Elaboration of this type of reaction to a major study of macromolecule formation in systems containing silicon, arsenic, and phosphorus with bridging oxygen, sulfur, and nitrogen groups has begun (160, 193). This work is not within the scope of the review.

Behavior in arsenic ( $As^{III}$ ) systems is rather similar thermodynamically to that in phosphorus ( $P^{III}$ ) systems, but comparable reactions were faster. Direct reaction calorimetry has been employed and kinetic data obtained by n.m.r. ( $H^1$  or  $F^{19}$ ) for rapid reactions. The only random system investigated so far is arsenic tribromide with arsenic trichloride. Transfer of radioactive arsenic ( $As^{76}$ ) from one halide to another (141) and Raman spectra (72) indicated random exchange of halogen. The halide mixture on distillation gave no pure halides. Three fractionations gave a clean separation of the starting materials, so that rapid disproportionation of the mixed halides at  $132^\circ$  must occur. An ionic mechanism has been proposed (141).



Exchange of arsenic trifluoride with other arsenic halides was not observed (72). Cryoscopy of arsenious acetate in arsenic bromide (m.p.  $36^\circ$ ) showed formation of extra species, presumably the monoacetate dibromide in excess solvent (102).



For exchange of alkoxy, alkylamino, or phenyl groups with halogen, enthalpies of  $1.7$ – $9$  kcal. mole $^{-1}$  showed the mixed product to be by far the most stable. Kinetically the phenylarsenic halides are rather stable, requiring high temperature ( $250$ – $300^\circ$ ) for disproportionation in contrast to the alkoxy or alkylamino exchange with chloride for which rate phenomena are rapid

TABLE XVII  
 REORGANIZATION OF C<sub>6</sub>H<sub>5</sub>, N(CH<sub>3</sub>)<sub>2</sub>, OCH<sub>3</sub>, F, Cl, AND Br SUBSTITUENTS DIRECTLY ATTACHED TO AS<sup>III</sup>

Temp., °C.	Equilibrium constants						
	A	B	K <sub>1</sub> <sup>a</sup>	Standard error	K <sub>2</sub> <sup>a</sup>	Standard error	Ref.
256	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Cl	5.7 × 10 <sup>-2</sup>				63
252	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Cl			5.9 × 10 <sup>-2</sup>		63
304	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Cl	7.0 × 10 <sup>-2</sup>		8.2 × 10 <sup>-2</sup>	0.2 × 10 <sup>-2</sup>	63
37	N(CH <sub>3</sub> ) <sub>2</sub>	F	ca. 10 <sup>-3</sup>	4 × 10 <sup>-6</sup>	1.6 × 10 <sup>-2</sup>	0.5 × 10 <sup>-2</sup>	133
37	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	0.095	0.004	0.314	0.012	133
37	OCH <sub>3</sub>	F	0.019	0.015	0.068	0.007	133
28	OCH <sub>3</sub>	F	0.0138	0.0008	0.080	0.003	133
37	OCH <sub>3</sub>	Cl	7.3 × 10 <sup>-4</sup>	0.6 × 10 <sup>-4</sup>	0.0859	0.001	133
37	OCH <sub>3</sub>	Br	0.016	0.003	0.009	0.003	133

<sup>a</sup> K<sub>1</sub> and K<sub>2</sub> have the same significance as in Table XVI, M = As<sup>III</sup>. <sup>b</sup> Chemical analysis used. Other data in this table obtained from n.m.r. work.

enough to be detected by n.m.r. spectra. Nonrandom equilibrium data are presented in Table XVII and kinetic details in Table XVIII.

Enthalpy data for these reactions (obtained directly) are compared in Table III with ΔG<sub>diff</sub> values calculated from K values in Table XVII. For these reactions, the equilibrium situation is far from random. The approximation ΔG<sub>diff</sub> = ΔH<sub>r</sub> is rather poor, ΔG<sub>diff</sub> being usually ca. 1–2 kcal. less than ΔH<sub>r</sub>. Where the equilibrium constants used are very large or very small or at high temperatures, the approximation has little value and an assessment of the TΔS term (perhaps from spectroscopic data) is necessary. Direct reaction calorimetry would be more satisfactory. Some problems of calorimetry in group V have been mentioned (144).

Reactivity in exchange with arsenic chloride is in the order As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ≪ As[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> < As(OCH<sub>3</sub>)<sub>3</sub> and AsF<sub>3</sub> ≪ As[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>. With trimethyl arsenite the order is As[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> ≪ AsCl<sub>3</sub> < AsBr<sub>3</sub> < AsF<sub>3</sub>. Trace impurities may have affected the short lifetimes in Table XVIII, and the authors placed no great credence in the absolute order of their data. However, rapid second-order reactions certainly occur between trimethyl arsenite or trisdimethylaminoarsine and arsenic halides with an activation energy of ca. 2 or 5 kcal. mole<sup>-1</sup> (NMe<sub>2</sub>) (133). For these reactions the halogen is apparently unimportant in comparison to the nucleophilic character of the oxygen or nitrogen attached to arsenic. This may reflect an electrophilic arsenic cation derived from halide as the active species. That phenyl-arsenic links are not readily cleaved by arsenic chloride emphasizes the importance of a nucleophilic transferring group in the activated complex.

An antimony bromiodide was isolated as a solid (32). The sharp melting point indicates that it was not a mixture of antimony tribromide and antimony triiodide. Equilibria with these compounds were presumably avoided in the solid state. No mixed halide was isolated on distillation of a mixture of antimony trichloride

TABLE XVIII

KINETIC DETAIL FOR REORGANIZATION REACTIONS ON AS<sup>III</sup>

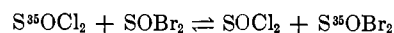
Temp., °C.	Second-order rate constants, k × 10 <sup>3</sup> , cc. mole <sup>-1</sup> sec. <sup>-1</sup>		Activation energy, kcal. mole <sup>-1</sup>	Activation entropy, e.u. (63)
	k <sub>a</sub>	k <sub>b</sub>		
252	k <sub>b</sub> = 0.89	k <sub>-b</sub> = 15.1	E <sub>b</sub> * = 37.6	ΔS <sub>b</sub> * = -2.88
256	k <sub>a</sub> = 3.22	k <sub>-a</sub> = 56.6	E <sub>-b</sub> * = 34.0	ΔS <sub>-b</sub> * = -4.26
304	k <sub>b</sub> = 22.7	k <sub>-b</sub> = 284		

Exchange lifetimes	τ, sec.	Temp., °C. (133)
As[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> + AsF <sub>3</sub> , AsCl <sub>3</sub> , or AsBr <sub>3</sub>	0.01	25
As(OCH <sub>3</sub> ) <sub>3</sub> + AsF <sub>3</sub>	0.005	25
As(OCH <sub>3</sub> ) <sub>3</sub> + AsCl <sub>3</sub>	0.07	25
As(OCH <sub>3</sub> ) <sub>3</sub> + AsBr <sub>3</sub>	0.03	25

and tribromide, and the chloride was cleanly separated at 225°. When one of the halides was labeled with radioactive antimony (Sb<sup>122</sup>), the label was found to be distributed randomly between the two halides after distillation of the mixture. Rapidly scrambling halogen, postulated as for arsenic, could explain these results (141). Ionic species in arsenic and antimony halides are much more credible than in phosphorus halides, but the nonreactivity of arsenic trifluoride, the most ionic arsenious halide, is difficult to reconcile with the ionization mechanism.

## E. GROUP VI

Although mixed halides of sulfur (sulfuryl chloride (81), thionyl chlorofluoride (106), and thionyl bromofluoride (42)) are known, they do not readily disproportionate and nothing is known of the equilibrium with the end halides. There is some evidence for chloride-bromide exchange in thionyl halides. Exchange of S<sup>35</sup> between thionyl chloride and thionyl bromide was found to be rapid in sulfur dioxide or thionyl chloride at -50°. Only in excess thionyl bro-



oxide was the reaction slow enough to investigate the rate ( $t_{1/2} = 80$  min.). No mixed halide was isolable but it must be an intermediate, either in an ionic or a four-center mechanism (105). An equimolar mixture of thionyl chloride and thionyl bromide had physical characteristics suggesting a rapid near-random halogen exchange (*i.e.*, a type a(i) reaction) from which only chloride or bromide could be obtained pure, despite an earlier report of isolation of mixed halide (125). In support of this interpretation, the mixed fluorohalides can be isolated. Fluorine has been found to exchange more slowly than the other halogens in halogen scrambling reactions (B, P, As) (46, 57, 72). The infrared spectrum of the thionyl chloride–thionyl bromide mixture would show the presence of any mixed halide (*cf.* the known sulfonyl halide spectra (81)).

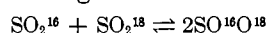
The slow exchange of central atom between its halides of two different oxidation states found for phosphorus was witnessed again here. Thionyl and sulfonyl halochlorides did not exchange  $S^{35}$  within 5 days at  $0^\circ$ . Ionic or four-center exchange of halogen could not result in sulfur exchange, as for halides in the same oxidation state. The intermediate must be the symmetrical adduct,  $Cl_2OS-O-SOCl_2$ , in which the stronger acid (sulfonyl chloride) has to act as oxide donor (or base) to the weaker acid; the authors suggested slow formation of this as the rate-determining step (105).

Solid mixed halides of tellurium (5, 6) and polonium (8, 9) have been reported ( $MCl_2I_2$  and  $MBr_2I_2$ ). The physical properties were not those expected for a mere mixture of appropriate tetrahalides. Disproportionation has not been investigated in mobile phases. The exchange of fluoride in sulfur, selenium, or tellurium tetrafluorides is, however, a rapid process at room temperature, and a discussion of possible intramolecular processes for this is included in section V. Selenium tetrafluoride has been postulated (95) to ionize in the following way.



An estimate (from temperature dependence of viscosity and conductivity) of the extent of ionization at  $25^\circ$  is 0.0133% (97). Rapid ionic exchange of fluorine (intermolecular path) may then be possible. Tellurium tetrafluoride is even more likely to be ionic.

Sulfur dioxide undergoes rapid oxygen exchange at room temperature. A sample containing heavy oxygen was allowed to exchange with one containing ordinary



oxygen, and the almost random mixture of these and the mixed oxide was inspected by infrared techniques. If isotope effects are neglected the statistical equilibrium constant  $K$  should be 4, experimental values of 3.2 and 2.9 were quoted. The exchange was complete in a few minutes both in the gas phase and in carbon tetrachloride solution. Sulfur dioxide was at one

time considered to ionize by oxide transfer but this can now be discounted as a mechanism (117). Trace water was not excluded as a possible catalyst, and exchange of oxygen in gaseous dioxide with the Pyrex vessel certainly occurred. A four-center mechanism is also possible (117).

Exchange of deuterium and hydrogen in water and aqueous ions is probably statistical (82). This should apply for deuterium and hydrogen exchange on other group VI hydrides, especially the more acidic ones.

#### F. GROUP VII

Halogen fluorides both alone and in admixture with other fluorides undergo rapid exchange of fluorine (33, 93). Ionic or associative mechanisms have been proposed for both, but recently intramolecular mechanisms have been suggested for the halogen fluoride alone. Surveys of these topics have been made (33, 136).

Iodine pentafluoride and bromine pentafluoride differed from the other halogen fluorides in requiring high temperatures for rapid halogen exchange (138). Activation energies were also higher than for halides of different symmetry, and the exchange was much less sensitive to impurities (93). Addition of potassium fluoride to iodine pentafluoride, which is thought to form the hexafluoroiodate (62), caused a rapid halogen exchange at room temperature (137, 186). This indicates an ionic mechanism in the salt solutions, but does not prove it for the pure solvent (for which, incidentally, the percentage of kinetically free ions at  $25^\circ$  has been estimated as 0.0034%) (97). The structure of these molecules (square-based pyramid) does not permit the molecular deformation which is supposed to account for rapid exchange in the other halogen fluorides.

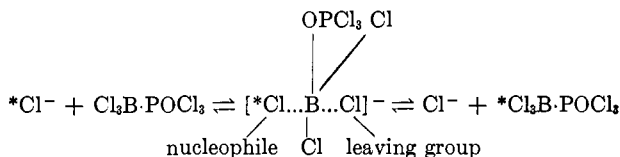
#### G. EXCHANGE BETWEEN TWO DIFFERENT CENTRAL ATOMS

Redistribution reactions of type a(iii) are very common. There is a large series of possible products although not all may be obtained under particular conditions. Consequently, thermodynamic and kinetic studies have been neglected. Where two central atoms are sufficiently different however, there is the possibility of isolating an intermediate in the exchange, and so we have a pointer to the mechanism. This has been done for several a(ii) reactions.

Phosphoryl chloride and boron trichloride form a 1:1 adduct of controversial structure. When boron trichloride was added to excess phosphoryl chloride containing radioactive chlorine, complete exchange of the label occurred in less than a minute. In excess boron trichloride, however, there was no chloride exchange after 43 hr. at  $0^\circ$ . The absence of exchange in the boron trichloride rich systems excluded an ionic intermediate  $POCl_2^+BCl_4^-$ . If the ionization



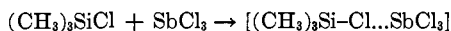
can occur in excess phosphoryl chloride, an  $S_N2$  attack of chloride on boron can account for the result. In excess boron trichloride, the phosphoryl trichloride would be present entirely as the adduct, and no radiochloride ion would be available for this mechanism (96).



Exchange of chlorine between phosphoryl chloride and group III chlorides other than boron was likewise found to be very slow unless additional halide ion was present. For instance, tetrachloroaluminate exchanged with phosphoryl chloride although aluminum chloride did not (116).

Rapid radiochlorine exchange occurred when a radioactive group III chloride was dissolved in nitrosyl chloride, in keeping with an ionic intermediate  $NO^+AlCl_4^-$  in which all chlorines become equivalent (116).

Trimethylchlorosilane and radioactive antimony trichloride exchanged chloride in a bimolecular reaction in benzene or hexane, but there were kinetic complications. Slow formation of a stable intermediate which increased the exchange rate was deduced from other kinetic experiments in which antimony trichloride and the silane were equilibrated for 36 hr., prior to addition of labeled antimony trichloride. The rate was approximately seven times greater (Table XIX).



The intermediate was required to involve coordination of the silyl chlorine to the antimony. A four-center mechanism between this intermediate and another molecule of antimony trichloride was suggested to complete the exchange (161).

TABLE XIX

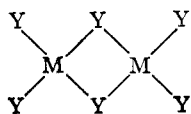
RATE OF RADIOCHLORIDE EXCHANGE (a) ON MIXING  
RADIOCHLORIDE AND SILANE DIRECTLY AND (b) ON ADDITION  
OF RADIOCHLORIDE TO AN EQUILIBRATED ANTIMONY  
HALIDE-SILANE MIXTURE<sup>c</sup>

Silane, <i>M</i>	Antimony halide, <i>M</i>	<i>k</i> <sub>2</sub> , l. mole <sup>-1</sup> sec. <sup>-1</sup> (40°)
a. 0.0198	0.0535	$7.5 \times 10^{-5}$
b. 0.0364	0.0747	$63 \times 10^{-5}$

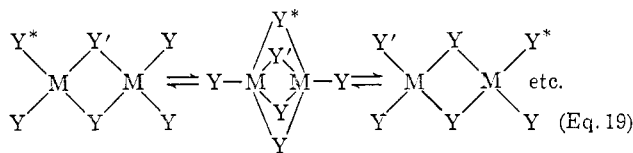
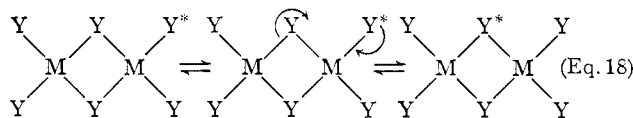
<sup>c</sup>  $E^* = 18.6 \pm 1.1$  kcal. mole<sup>-1</sup>;  $\Delta S^* = 18 \pm 4$  e.u.

## V. INTRAMOLECULAR EXCHANGE

Intramolecular exchange appears as a mechanism in group III. In various dimeric structures typical of group III such as



the bridging Y groups should differ from the terminal groups spectroscopically, and observation of the spectroscopic nonequivalence of bridging and terminal groups at one temperature, but equivalence of all six at higher temperatures, has been taken as evidence of exchange. For such exchange in dimeric trimethylalane, the mechanism is unlikely to be dissociation to monomeric fragments, as the enthalpy of this dissociation is known to be 20.2 kcal. mole<sup>-1</sup>, but the activation energy for the exchange process, measured by n.m.r. methods, is about half of this (see Table XX). Intramolecular processes such as Eq. 18 and 19, rendering the six methyl groups equivalent, were invoked (140).



This type of mechanism cannot account for the spectroscopic equivalence of methyl groups in methylaluminum dichloride and dimethylaluminum chloride mixtures at 25° (20), for which some authors favor ionic exchange of chloride (80). Rapid intermolecular exchange of ethyl groups between triethylalane and diethylaluminum chloride occurred simultaneously with even faster intramolecular exchange (183) of ethyl in the triethylalane.

Diborane and various amino-bridged derivatives have been investigated *via* their B<sup>11</sup> resonance in ether solutions, and intramolecular exchange is thought to occur by ether coordination to boron followed by bridge bond fission and rotation as in Eq. 18 above (74, 75). By similar arguments to that for trimethylalane, dissociation of diborane to monomeric fragments seems an unlikely mechanism. The activation energy for exchange of bridge and terminal protons in ether was found to be 4.8 kcal. mole<sup>-1</sup> (74), but for the gas phase exchange of deuterium between diborane and perdeuteriodiborane (presumably by dissociation to monomer), an activation energy of 21.8 ± 3 kcal. was found (124). Likewise the gas phase exchange of deuterium between diborane and  $\mu$ -dimethylaminoborane had an activation energy of 27.8 ± 3 kcal. compared to the 3.7 kcal. required to render the protons in dimethylaminodiborane solution equivalent (75). The extrapolation of these gas phase figures to ether solutions may of course not be viable. The exchange was too slow to be observed by the n.m.r. technique in gaseous diborane (74) but was partly observable in dimethylaminodiborane (155, 199, 200).

Present indications are that halogen exchange of a rather different nature to that discussed previously can occur in group V, VI, and VII fluorides. It is probably intramolecular, involving deformation of the molecule, but differs from the group III mechanisms in that no bonds are broken. Sulfur and selenium tetrafluorides are known to have  $C_{2v}$  symmetry (7, 190) with two non-equivalent sets of fluorines in the molecule. At room temperature the n.m.r. spectrum of each shows only one type of fluorine and the expected fine structure of the spectrum is only observed at low temperatures. These data indicate an exchange of fluorine between axial and equatorial positions in the molecule. The original interpretation of bimolecular exchange based on solvent effect on rate was superseded by one involving a pseudo-rotation of the molecule (135). The barrier to this rotation for sulfur tetrafluoride has been estimated (26), in reasonable agreement with the experimentally observed activation energy for exchange (see Table XX). A possible ionic mechanism for selenium tetrafluoride was considered in section IVE.

Similar investigations on group V and group VII halides based on the same trigonal bipyramid structure indicate that rapid exchange of groups between axial and equatorial positions occurs (135, 136). For iodine heptafluoride, probably a pentagonal bipyramid, n.m.r. equivalence of groups has also been observed and a case for pseudo-rotation made (139). No such pseudo-rotation is possible for the square-pyramidal iodine pentafluoride and bromine pentafluoride discussed in section IVF. Activation energies for fluorine exchange determined from n.m.r. data are collected in Table XX.

TABLE XX

ACTIVATION ENERGIES FOR POSITIONAL EXCHANGE			
Compound	Solvent	$E^*$ , kcal. mole <sup>-1</sup>	Ref.
B <sub>2</sub> H <sub>6</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	4.8 ± 1.5	74
(CH <sub>3</sub> ) <sub>2</sub> NB <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	3.7	75
Al <sub>2</sub> (CH <sub>3</sub> ) <sub>6</sub>	Liquid	6-14	140
CH <sub>3</sub> AlCl <sub>2</sub> + (CH <sub>3</sub> ) <sub>4</sub> Al <sub>2</sub> Cl <sub>2</sub>	Liquid	12 <sup>a</sup>	20
Tl(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	6 ± 1 (inter-molecular)	123
(CH <sub>3</sub> ) <sub>4</sub> PF <sub>3</sub>	Liquid	ca. 7	135
SF <sub>4</sub>	Liquid	4.5 ± 0.8	137
		5-10 (calcd.)	26
ClF <sub>3</sub>	Liquid	4.8	138
IF <sub>5</sub>	Liquid	13	138

<sup>a</sup> Possibly inter- and intramolecular (87, 183).

A cyclic phosphorane (CH<sub>3</sub>)<sub>4</sub>PF<sub>3</sub> exhibits spectroscopic equivalence of fluorine at 25°, but F<sup>19</sup>-H<sup>1</sup> and F<sup>19</sup>-P<sup>31</sup> spin coupling are retained. The complete spectrum demonstrating the presence of axial and equatorial fluorine is observed at temperatures below -70°. Rapid intramolecular stereochemical exchange must be postulated to explain the retention of spin coupling. The six-membered ring (CH<sub>3</sub>)<sub>5</sub>PF<sub>3</sub> does not undergo this exchange below 100° (135).

Compounds most sensitive to exchange with fluorine-containing impurities may in fact undergo catalyzed

intermolecular exchange. Their reactivity makes it very difficult in practice to obtain extremely pure samples for analysis, and the information given in Table XX for chlorine trifluoride has been criticized on these grounds (93). Intramolecular exchange is not fully established except for the phosphorane, some group III compounds, and perhaps sulfur tetrafluoride.

## VI. TRENDS IN INTERMOLECULAR REACTIONS

Any intermolecular exchange (redistribution reaction) can be characterized completely if its thermodynamic and kinetic parameters have been evaluated. For most reactions this is either impossible or not yet accomplished. Trends in the reactions already cited should be useful in prediction of exchange characteristics.

### A. THERMODYNAMIC

For the first type of reaction mentioned, a(i), random exchange is never attained. That is, there is always some heat of reaction. When the exchanging groups X and Y are of the same type (*e.g.*, both halogen, or ester or amino or alkyl), their eventual distribution between mixed and end components is close to random. This can be seen in values of  $K$  close to the statistical one or in low enthalpies of reaction for elements M as different as Hg, C, Pb, or O and exchanging groups X = Y = H, halogen, ester, alkylamino, or alkyl. A notable exception is the exchange of methyl and ethyl groups on boron which appears to favor the end compounds entirely, although this circumstance is not repeated in the butyl-propyl exchange (131). When X and Y are different types of group, *e.g.*, X = halogen and Y = ester, the equilibrium departs further from random, and sizeable enthalpies are found. Several authors (67, 197) have noted a similarity in magnitude of redistribution enthalpy for the same groups X and Y scrambling on a series of central atoms (M = B, Si, P, As). Relevant data are collected in Tables II and III. Some of the enthalpy data were approximate only, as discussed earlier. Resemblance for exchange of halogen-halogen, alkoxy-halogen, and dialkylamino-halogen is indeed striking. For boron, silicon, and phosphorus, which have electronegativities close to 2, the resemblance is greatest. Although the bond energies B-X, Si-X, and P-X are not the same, the variation in, say, Si-Cl bond energy from the molecule SiCl<sub>4</sub> to (CH<sub>3</sub>O)<sub>3</sub>-SiCl cannot be very different from the bond-energy variation for B-Cl between BCl<sub>3</sub> and (CH<sub>3</sub>O)<sub>2</sub>BCl. The enthalpy data for exchange of methyl and halogen on mercury or tin are in the same direction (favoring the mixed compound) but are very different in magnitude. The extrapolation of redistribution enthalpy from one central atom to another would thus not be justified on the data of Table II, although it may well give a good approximation for boron, silicon, or phos-



phorus or other closely related groups of elements. Further accumulation of enthalpy data is necessary before any confident predictions of reactivity for very electropositive or electronegative M can be made.

The n.m.r. chemical shift for a particular atom M in Eq. 2 is different in compounds  $MA_n$ ,  $MA_nB_j$ , and  $MB_n$ . Van Wazer has noted that where Eq. 2 denotes a near-random exchange, chemical shifts vary linearly from  $MA_n$  through  $MB_n$  (193). When the exchange was not random, shifts were found to be nonlinear. This finding for phosphorus compounds has been confirmed for some boron compounds (38, 113). As n.m.r. methods are frequently simpler to apply than calorimetric ones, it may be that this relationship could be used to predict equilibrium for specific reactions, but again more data are required to test the hypothesis.

### B. KINETIC

Rate in reactions of type a(i) varies with M. The trends are not all clear, but the most electropositive M within a group exchanges fastest. Within groups the tendency is  $Sn > Ge > Si > C$ ;  $Tl > Al$ ;  $As > P$  for such reactions as have been studied. Trends from group to group are not so clear but exchange rates are in the approximate order  $III > IV > V$  (trivalent)  $> V$  (pentavalent). Coordinatively saturated structures like carbon tetrachloride or sulfur hexafluoride exchange ligands very slowly if at all. Exchange of a central atom from one oxidation state to another (*i.e.*, an oxidation-reduction reaction) was very slow (for S and P) in comparison to exchange between two compounds in the same oxidation state.

Rate is also dependent on the nature of X or Y. Where X and Y are of the same type, *e.g.*, halogen, exchange rates decrease in the order  $X = Y = \text{halogen} > \text{ester} \sim \text{amino} > \text{methyl}$ . Within the halogen series,  $F < Cl < Br$  for  $M = B, As^{III}, \text{ or } P^{III}$ , and  $OCH_3 > OC_6H_5$  (on  $P^{III}$ ). When X and Y are of different types, the reaction rate may be faster than an exchange of X with X or Y with Y, or intermediate between them, but so far no rate slower than either has been found. Amino-halogen exchange is very fast at room temperature for  $M = B, Si, P, \text{ and } As$  in comparison to slower alkylamino exchange on boron, or halogen exchange on silicon or phosphorus. Ester-halogen exchange was likewise faster than ester-ester or halogen-halogen exchange (for phosphorus and silicon). The aryl-halogen exchange, studied for mercury and arsenic was intermediate in rate between very slow or unobserved aryl-aryl exchange and room temperature halogen exchange.

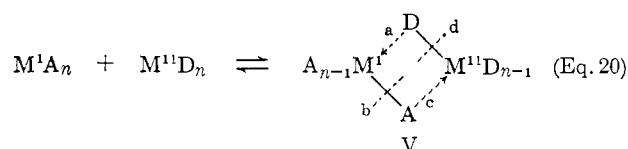
### C. MECHANISTIC

Mechanisms proposed so far are (1) free-radical dissociation of reactants, (2) the four-center ( $S_F2$  or  $S_{Ei}$ ) mechanism, (3) electrophilic substitution, (4) nucleophilic substitution, and (5) stepwise complex formation.

### 1. Free-Radical Reactions

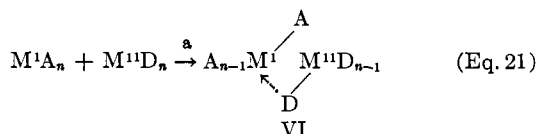
Breakdown of a molecule to radical fragments and recombination after reshuffling is undoubtedly a common route for redistribution especially at high temperatures in the gas phase. However, most of the redistribution reactions on main-group elements so far studied show no sign of radical intermediates. Their presence should be signaled particularly by isolation of other products such as ethane from a methyl-metal bond rupture and fluorinated hydrocarbons from a sulfur-fluorine bond fission. Such side products were not observed in the scrambling of alkyl groups on tetramethyl plumbane at moderate temperatures (13, 24) or the exchange of fluorine on sulfur tetrafluoride in various solvents (137).

### 2. Four-Center Mechanisms



In this mechanism we anticipate that the transition state depicted (V) would be most readily attained for central atoms M with strong electron-acceptor character and exchanging groups A and D with strong donor character. It must be remembered, however, that these characteristics are conflicting; that is, strong donor power of A and D will tend to reduce the accepting power of the central atom M and, on the other hand, strong acceptor character of M will reduce the donor strength of A and D. The breaking and forming of bonds in this transition state are depicted as effectively simultaneous. Intermediates of this type have been suggested for most redistribution reactions. For reaction of compounds for which bridge dimers are stable (*e.g.*, intermolecular exchange of trimethylboron with diborane to give methylboranes) such intermediates are reasonable. Fission of one bridge bond apparently occurs in many such dimers leading to intramolecular exchanges (see section V), and so a metastable intermediate in the intermolecular reaction with, say, bond  $M^I-A$  broken is also possible. The actual transition state, *i.e.*, point of highest energy in the reaction, must be the second bond fission ( $M^{II}-D$ , say, in this example).

For reactions where dimeric species have not been detected, but rapid exchange occurs, *e.g.*, scrambling of halogen on tin, some readily available transition state is indicated. A sequence of steps can be rationalized here also. The steps labeled a, b, c, and d in V may occur in any order. If a bridge dimer is formed then the order is a and c followed by b and d. Another rational order is first a, that is nucleophilic attack of donor D on acceptor  $M^I$  (VI). In this intermediate,  $M^I$  should have



reduced acceptor power and  $M^{11}$  should have increased acceptor power, while the bond  $M^1-A$  is sufficiently weakened to increase the nucleophilicity of A. Step c, the formation of the  $M^1-A$  bond is thus facilitated. Bond-fission steps b and d would give products, or a and c would regenerate reactants. If  $M^1$  is a better acceptor than  $M^{11}$  and D is a better donor than A, this sequence seems likely. For the reactions we have seen to be most rapid, these conditions are met, *e.g.*, tetrakisdimethylaminosilicon and silicon tetrachloride being  $M^{11}D_n$  and  $M^1A_n$ , respectively, react faster than two silicon halides. The mechanism has been confirmed by kinetic salt effects for the alkylmercury halide-mercuric halide exchange.

The fact that scrambling on good acceptor atoms of good donor groups is rapid is in accord with this sequence. Central atoms with no acceptor tendencies like carbon in carbon tetrachloride and sulfur in sulfur hexafluoride do not undergo scrambling reactions readily. Methyl groups would be expected to have low reactivity on this mechanism and results bear this out except for reactions of trimethylaluminum where there is special bonding of methyl as a bridging group, the related thallium reactions, and dimethylmercury reactions for which a different mechanism has been proposed. Slow transfer of the phenyl group likewise may be ascribed to its lack of donor ability. Reaction of tetraphenyltin with tin tetrachloride occurs on refluxing, but the reaction of the stronger Lewis acid boron trichloride is faster (34, 78). Halogens, having both donor character and high electronegativity, exchange rapidly on good acceptor atoms.

For type a(ii) and a(iii) reactions, the intermediate of step a (Eq. 21) may be isolable, as was noted in section IVG for silyl chloride-antimony chloride exchange of chlorine (161).

Catalysis by group III compounds is obviously applicable on this mechanism, the Lewis acid scrambling rapidly with both major components of the exchange. Intermediates have been isolated confirming this role of the catalyst (23, 24).

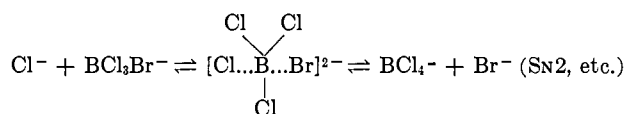
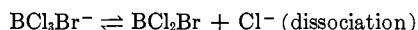
### 3. Electrophilic Substitution

If the central atom is rather metallic and the attached groups are readily ionized, then electrophilic attack is a possible rate-determining step of the reaction (stepwise complex formation is also possible here, see section 5). The difference from a four-center mechanism is merely in the timing of heterolysis and bond formation as in Eq. 20. The first and rapid step is ionization of the most ionic bond, let us say  $M^1-A$ .

The electrophilic character of  $M^1$  is now increased and reaction with nucleophilic D follows (step a, Eq. 20). The successive steps d and c are expected to be fast. This  $SE_2$  mechanism was apparently observed for many of the mercury exchanges described in section IVA. An  $SE_1$  mechanism was also observed for a mercury reaction in an aqueous solvent.

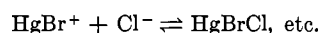
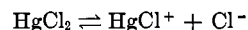
### 4. Nucleophilic Substitution

A rapid dissociation step might give a powerful nucleophile, as for instance in tetrahaloborates.  $SN_2$  attack of halide on another molecule of tetrahaloborate can then occur as below. An alternative mechanism is shown in the next section.

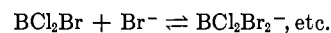


### 5. Stepwise Complex Formation

Dissociation followed by rapid reassociation with a different ligand is a simple picture which probably applies for exchange between two potentially ionic salts such as mercury chloride and bromide in aqueous solution.



For the tetrahaloborate exchange it is an alternative to nucleophilic substitution.



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