zero point energies for the normal and expanded lattices should be even smaller.

The sum of the van der Waals energy and the inductive energy is 19.2 kcal./mole. This value subtracted from 50.5 kcal./mole is the estimate of the charge-transfer energy between the silver ions and the benzene molecules (Table III). This 31.3 kcal./mole represents the energy of a silver ion bonded to two benzene molecules; therefore, the energy per bond is 15.7 kcal./mole.

Although the errors involved in these calculations are probably large, most of the more uncertain quantities, such as van der Waals and induction terms, are relatively small and tend to cancel for the two step process used in the calculation. The Madelung energy difference between the expanded and normal AgClO$_4$ structures is probably quite accurate and is the principal term. The authors believe these results are more reliable than the rough estimate of 50 kcal./bond mole by Tiddlesby and Sharpe.[12] Their value is based upon the questionable assumption that most of the lattice energy of silver perchlorate is lost in forming the charge-transfer complex, a result dependent upon estimating ion pair interactions in solution. This estimate is surely of less accuracy than the Madelung energy difference computed here.

The charge-transfer bond energy found in this investigation is of the order of the van der Waals and induction energies in agreement with Mulliken's prediction of the magnitude of the charge-transfer interaction.

Acknowledgment.—The authors are indebted to Dr. D. Templeton of the University of California for the least squares program used in refinement and to Mr. D. R. Fitzwater for aid in making the program work on the local computer.

AMES, IOWA

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Isotopic Exchange Reactions. IV. Evidence for the Tetrachloroborate Anion from Kinetic Studies[1]

BY ROLFE H. HERBER

RECEIVED APRIL 28, 1958

The halogen exchange between BCl$_3$ and a number of chloride salts has been studied in both the liquid and gas phase using Cl^{36} as a radiotracer. The heavy alkali metal salts do not undergo exchange at 0° in several hours. LiCl shows a small amount of halogen transfer in liquid BCl$_3$. Both (CH$_3$)$_4$NCl and (CH$_3$CH$_2$)$_4$NCl solutes exchange chlorine rapidly with liquid BCl$_3$ and the exchange with the former has been exploited to prepare radiochlorine labelled BCl$_3$. Silicon tetrachloride and trimethylchlorosilane do not exchange halogens with BCl$_3$ in the gas phase, although the latter should form a 1:1 addition compound with boron trichloride. These results are interpreted on the basis of an ionic mechanism which involves the formation of the tetrachloroborate anion in BCl$_3$ solution.

In a recent communication,[2] Muetterties has reported the preparation of a number of alkali metal salts of the unknown tetrachloroboric acid, HBCl$_4$. KBCl$_4$, RbBCl$_4$ and CsBCl$_4$ were recovered from a reaction vessel heated to 400 to 500° for 0.5 hr. and then cooled over a period of 8 hr. During this cooling period, the alkali metal salt was presumably in contact with liquid BCl$_3$, and hence the metathesis may have taken place either under gas–solid or liquid–solid heterogeneous reaction conditions. These results are of considerable interest in their relation to studies of isotopic exchange reactions of several volatile inorganic halides being carried out in this Laboratory, especially to work involving liquid and gaseous BCl$_3$.

The present study was undertaken to explore the possibility that BCl$_4^-$ may be a reactive intermediate in isotopic exchange reactions of BCl$_3$, and to elucidate the conditions under which this anion may be formed.

Experimental

Tetramethylammonium Radiochloride.—The chlorine labeled reagent was prepared by dissolving E. K. white label grade salt in a minimal volume of water, adding an aliquot of HCl^{36}[3] and evaporating to dryness under high vacuum conditions. Subsequent pumping on this (and the following) salt while warmed to 100° was continued until static vacua of 10 μ or less were attained in all cases except the tetraethylammonium chloride, which has an m.p. of 37.5°.

Tetraethylammonium Radiochloride.—The unlabeled salt was prepared by neutralizing an aqueous 10% solution of Eastman Kodak tetraethylammonium hydroxide with HCl and evaporating to dryness. The chlorine labeled salt was prepared as above.

Alkali Metal Halides.—Lithium, rubidium and cesium chloride salts were reagent grade chemicals used without further purification. Chlorine-36 labeling was carried out as above.

Boron Trichloride.—Matheson 99% BCl$_3$ was freed of permanent gas impurity by alternate freezing, pumping and liquefaction cycles under high vacuum conditions. HCl was removed by warming the BCl$_3$ to −78° and pumping. Middle fractions of the purified gas were stored in glass ampoules. Chlorine-36 labeled BCl$_3$ was prepared from tetramethylammonium radiochloride on the basis of the results of the present work.

Chlorosilanes.—Silicon tetrachloride and trimethylchlorosilane were General Electric Co. reagents. Chlorine-36 labeled silanes were prepared as detailed in a previous communication.[4]

Exchange Run Procedure.—The experimental method used to follow the isotopic exchange kinetics was essentially that employed in previously reported[5] work. The gas-phase exchange runs (using SiCl$_4$ and (CH$_3$)$_3$SiCl) were carried out in 300-cc. Pyrex reaction flasks. The reactants were maintained at 24.0 ± 0.5 or 30.0 ± 0.5° in a water-bath and complete volatilization was noted within 10 seconds. Separation of BCl$_3$ from the chlorosilanes for radioassay was effected by cooling the reactants in a slush bath of *n*-hexanol (−50°). Since the vapor pressures of SiCl$_4$ and

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[1] This work supported by the U. S. Atomic Energy Commission. Presented in part as paper 132, Division of Physical Chemistry, San Francisco Meeting Am. Chem. Soc., April, 1958.

[2] E. L. Muetterties, THIS JOURNAL, **79**, 6563 (1957).

[3] Item Cl-36-P, available from Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[4] R. H. Herber, *J. Phys. Chem.*, **62**, 379 (1958).

[5] R. H. Herber and A. W. Cordes, *J. Chem. Phys.*, **28**, 361 (1958).

$(CH_3)_3SiCl$ are about 4 mm. at this temperature, a small, incomplete separation factor correction was applied in the radioassay of the BCl_3 aliquots. The heterogeneous experiments (alkali metal salts, $(CH_3)_4NCl$ and $(CH_3CH_2)_4NCl$) were carried out in 25-cc. Pyrex test-tubes fitted with stopcocks and standard taper joints for attachment to the vacuum manifold.

The experiments designed to test the homogeneous/heterogeneous nature of the $(CH_3)_4NCl$ exchange (see below) were carried out in an H-shaped reaction assembly constructed of Pyrex glass. The cross arm was partitioned by a "C" grade glass sintered filter, while the tops of the two vertical segments were fitted with stopcocks and standard taper male joints for attachment to the vacuum manifold. The bottom of each vertical segment was sealed to a test-tube end. In these experiments, chlorine-36 labeled tetramethylammonium chloride was introduced as an aqueous solution into one arm of the apparatus *via* a side arm which was then sealed off. The excess water and HCl were removed by evaporation and the salt finally subjected to high vacuum pumping while warmed to 100° until a static vacuum of less than 20 μ was attained. Anhydrous, HCl-free boron trichloride was dosed into the same arm of the assembly, using liquid nitrogen as the refrigerant. The BCl_3–$(CH_3)_4NCl$ condensate was then warmed to 0° with an ice-bath for known time intervals, and samples of BCl_3—constituting the "heterogeneous phase" of the reaction—removed for radioassay and then returned to the reaction apparatus. The saturated BCl_3 solution was filtered by closing the appropriate stopcocks and rotating the apparatus through 90° so that the suspension flowed into the side arm. Gradual cooling of the second vertical segment caused the liquid phase to pass through the glass filter, leaving the solid residue of the chloride salt behind. Inspection of the solution subsequent to filtration showed a clear liquid, with no evidence for suspended particles of the ammonium salt. After maintaining the clear solution at 0° for known time intervals, samples of BCl_3 were again removed for radioassay and returned to the reaction system by distillation. These samples constituted the "homogeneous" phase of the reaction. Subsequently, the BCl_3 was *distilled* through the glass filter back into the original reaction compartment, leaving a slight white residue, indicating the presence of solute $(CH_3)_4NCl$ in the original filtrate.

Experimental Results

Exchange Runs with $SiCl_4$ and $(CH_3)_3SiCl$.—The homogeneous gas-phase halogen exchange between BCl_3 and $SiCl_4$ was studied at 30°, using $SiCl_3Cl^{36}$ and initially unlabeled boron trichloride. No growth in the activity of the BCl_3 fraction was observed, even after 24 hours. To confirm the absence of exchange, the two reactants were completely separated and the specific activity of the $SiCl_4$ fraction redetermined. These were 12.7 and 12.8 c.p.m./cm. after 24 and 1440 minutes, respectively, and are essentially identical to the initial $SiCl_4$ specific activity of 12.9 c.p.m./cm. The specific activity expected for complete exchange was 10.1 c.p.m./cm. A similar gas-phase exchange run was carried out using 0.786 mmole of $(CH_3)_3SiCl^{36}$ (70.4 c.p.m./cm.) and 2.07 mmoles of BCl_3 at 24°. No exchange of halogens between the silane and BCl_3 was observed in 1250 minutes. The withdrawal of 9 samples of BCl_3 for radioassay from liquid silane over this time interval did not result in separation induced exchange.

Exchange Runs with RbCl, CsCl and LiCl.—These exchange runs were carried out at 0° to ensure the presence of liquid BCl_3 (b.p. 12.5°). In each case the presence of undissolved salt was confirmed during the exchange run. In the case of $RbCl^{36}$, 0.991 mmole of the salt and 1.88 mmoles of BCl_3 were used. No growth of chlorine activity in the latter was observed, even after 950 minutes. In the case of $CsCl^{36}$, using 1.004 mmoles of the salt and 4.36 mmoles of BCl_3, again no growth of activity in the latter was noted after 2760 minutes.

Some transfer of activity to the BCl_3 fraction was observed in an exchange run using $LiCl^{36}$ at 0°. Here, 2.04 mmoles of the salt and 1.84 mmoles of BCl_3 were contacted for times up to 2450 minutes. Representative specific activities of the BCl_3 fraction are: 0.047 c.p.m./cm. after 1 min., 0.881 c.p.m./cm. after 60 min., 2.526 c.p.m./cm. after 1435 min., and 3.212 c.p.m./cm. after the full interval.

Exchange Runs with $(CH_3)_4NCl$.—A number of exchange runs with chlorine-labeled salt were carried out, since this material had been found in an earlier study[4] to provide an efficacious path for preparing chlorine labeled $SiCl_4$. In a typical experiment, 2.5 mmoles of BCl_3 was transferred to a reaction tube containing 0.82 gram of $(CH_3)_4NCl^{35}$ (7.5 mmoles) and the reaction system warmed to 0°. The specific activity of the BCl_3 fraction as a function of time, normalized to the extrapolated infinite time specific activity (S_t/S_∞), is shown in Fig. 1. Specific activities as high as 130 c.p.m./cm. (H_2SO_4) (corresponding to 960 c.p.m./cm. (Hg)) of BCl_3 have been routinely obtained, and exchange with chlorine-labeled $(CH_3)_4NCl$ thus provides a convenient method of introducing the tracer halogen into BCl_3.

Exchange Run with $(CH_3CH_2)_4NCl$.—A single exchange experiment, using 6.0 mmoles of the labeled salt and 2.2 mmoles of BCl_3, was carried out at 0°. Again, a rapid growth of specific activity of the BCl_3 fraction was noted, and the normalized activity data are also plotted in Fig. 1.

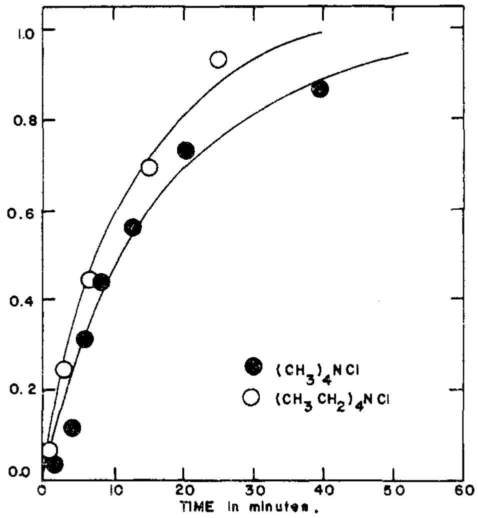

Fig. 1.—Quaternary ammonium salt–boron trichloride exchange.

Test of Reaction Heterogeneity.—Using the procedure detailed in the Experimental section of this paper and the filtration apparatus described above, an exchange run between 2 mmoles of chlorine-labeled $(CH_3)_4NCl$ and 12.6 mmoles of BCl_3 was carried out at 0°. The large excess of the latter was used to ensure sufficient solution volume for filtration. The growth of activity in the BCl_3 fraction is shown in Fig. 2. Aliquots assayed dur-

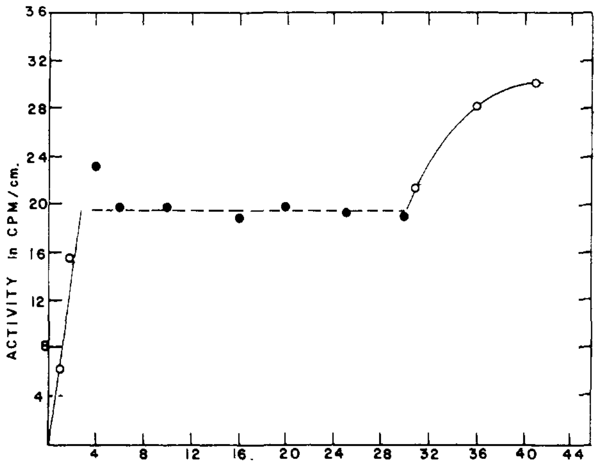

Fig. 2.—Test of homogeneity of the $(CH_3)_4NCl \cdot BCl_3$ exchange.

ing the "heterogeneous" part of the experiment are represented by open circles, while aliquots representing the filtered solution, and hence the "homogeneous" portion of the experiment, are indicated by closed circles. Essentially no change in the specific activity of the BCl_3 was noted during the "homogeneous" phase of the exchange run.

To ensure that catalysis of a possible slow homogeneous solution phase reaction by the presence of the excess solid salt in the "heterogeneous" segment of the filtration apparatus was not a significant factor in the observed results, a second experiment was carried out. A small amount of CsCl, which had been shown not to undergo halogen exchange with BCl_3 (see above), was placed into the "homogeneous" segment, and an exchange run between labeled $(CH_3)_4HCl$ and BCl_3—including the filtration step—was carried out. Again, activity growth in the BCl_3 fraction was noted only when liquid boron trichloride was in contact with the chlorine-labeled ammonium salt in the "heterogeneous" segment, showing the absence of catalysis of a possible solution reaction by the presence of the solid salt.

Discussion

As has been pointed out by Lévy and Brockway[6] the bonding in tetra-substituted boron compounds should be sp^3, and thus in the free anion, four homoatomic ligands should be kinetically equal. If the formation of the reported[2] alkali metal tetrachloroborates proceeds *via* the formation of such an anion during the "cooling period," an exchange path becomes available for transfer of chlorine activity from the alkali metal salts to BCl_3. From the absence of observed exchange between RbCl and CsCl and BCl_3—which Muetterties cites as the most reactive of the alkali metal salts—it may be inferred that no significant concentrations of BCl_4^- are established under the present conditions, that is, at 0°. The small amount of exchange observed in the case of LiCl suggests that a solubility limitation may be operative, since this salt should be more soluble in liquid BCl_3 than RbCl or CsCl due to its greater covalency. The formation of the heavier alkali metal tetrachloroborates may, of course, still proceed *via* the formation of a BCl_4^- anion, but if so, only at higher temperatures when the BCl_3 solubility of such salts may be significantly greater.

Still more soluble are the quaternary ammonium halides and for these, a rapid halogen activity transfer to solvent BCl_3 is noted. If the solubility consideration is correct, there are two possible explanations of the measurable exchange rates: (a) the observed exchange is the natural rate of a homogeneous reaction between dissolved salt and solvent BCl_3 (*i.e.*, $MCl^{36} + BCl_3 \rightleftarrows MCl + BCl_2Cl^{36}$); or (b) the exchange rate is governed by crystal growth and solution due to temperature gradients and/or migration of chloride ions to the surface of the chloride salts, exchange occurring by virtue of equilibrium between BCl_4^- and ionized solute (*i.e.*, $Cl^{36-} + BCl_3 \rightleftarrows BCl_3Cl^{36-}$). In the subsequent discussion, (a) will be termed the atom transfer path, and (b) the ionic path. It is suggested that a decision between these two mechanisms can be made on the basis of the filtration experiment, the data of which are summarized in Fig. 2. Increase in BCl_3 activity is noted only when solvent BCl_3 is in contact with solid salt, while the saturated, filtered solution shows constant specific activity. From these data it may be concluded that halogen activity transfer is *via* the suggested ionic path in which the formation of the tetrachloroborate anion proceeds through a very rapid ionic equilibrium.

These results do not imply that under suitable conditions an atom transfer process may not also provide for halogen exchange with BCl_3. Indeed, other work in this Laboratory has shown that homogeneous gas phase isotopic halogen exchange between HCl and BCl_3 is rapid at 24°, presumably occurring by such a non-ionic mechanism. From the present work, however, it may be concluded that atom transfer mechanisms are not important in the case of ionic chloride solutes in BCl_3.

In this connection, similar studies by Guttmann[7a] and Lewis and Sowerby[7b] with arsenic trichloride have shown that the formation of solvates of the type $(CH_3)_4NAsCl_4$ is reflected in a rapid halogen exchange between the ammonium salt and solvent $AsCl_3$. In the present studies the formation of analogous tetrachloroborate solvates, even if only in stoichiometrically minute amounts, would be in agreement with the observed results. Also pertinent in this context is the reported[8] dissociation of $(CH_3CH_2)_4NCl$ into ions in liquid $SOCl_2$ as well as the demonstrated[9] rapid halogen exchange between solvent $SOCl_2$ and $(CH_3)_4NCl$, presumably *via* an ionic reaction path.

It may also be noted that the formation of a 1:1 addition compound between BCl_3 and $(CH_3)_3SiCl$ (for which a dipole larger than 1.28 *D* is cal-

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(6) H. A. Lévy and L. O. Brockway, This Journal, **59**, 2085 (1937).

(7) (a) V. Guttmann, *Z. anorg. allgem. Chem.*, **266**, 331 (1951); (b) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957).

(8) H. Spandau and E. Brumeck, *Z. anorg. allgem. Chem.*, **278**, 197 (1955).

(9) B. J. Masters and T. H. Norris, This Journal, **77**, 1346 (1955); T. H. Norris, private communication.

culated from the data of Curran, *et al.*[10]) postulated from the work of Martin,[11] does not result in a rapid halogen activity transfer between the two halides, since this would have been observed under the conditions of the present exchange runs.

The absence of exchange in the homogeneous gas phase between the two chlorosilanes tested and BCl_3 also appears to be in consonance with the suggested ionic exchange mechanism. It may be further noted that absence of halogen exchange between $SiCl_4$ and BCl_3 is in agreement with the previously reported[5,12] exchanges of silicon tetrachloride in which absence of halogen transfer between $SiCl_4$ and symmetrical covalent chlorides was predicted.

Acknowledgments.—The author is indebted to Mr. C. T. Bishop and Miss S. C. Chang for assistance in the present work and to his colleague, Prof. L. A. Hiller, Jr., for helpful discussions of the exchange mechanisms proposed.

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[10] C. Curran, R. M. Witucki and P. A. McCusker, THIS JOURNAL, **72**, 4471 (1950).

[11] D. R. Martin, *J. Phys. Colloid Chem.*, **51**, 1400 (1947).

[12] R. H. Herber, *J. Chem. Phys.*, **27**, 653 (1957).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Reactions of Triethylsilane and Diethylsilane with Inorganic Halides and Acids

BY HERBERT H. ANDERSON

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Triethylsilane reduces certain halides or sulfates of at least 10 transitional elements and 5 elements in regular groups either to a lower oxidation state or sometimes to the free element. Oxidation of triethylsilane primarily to hexaethyldisiloxane occurs with a deficiency of 100% sulfuric acid or with 15 *M* nitric acid or chlorosulfonic acid. Table I lists 24 reactions of triethylsilane, with a median yield of approximately 81%. In a new modification, diethylsilane and a deficiency of mercuric bromide yield new diethylbromosilane. Other new compounds include diethyliodosilane and *sym*-tetraethyldisiloxane. As before, the two main explanations for the reaction of triethylsilane with a given halide depend on heats of formation per equivalent of available halogen in the compounds and on the appropriate ionization potentials of the elements.

Earlier papers establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to germanium[1] in $(C_2H_5)_3GeH$ or to tin[2] in $(C_2H_5)_3SnH$. This paper, in turn, studies the similar replacement of hydrogen attached to silicon in the exactly analogous $(C_2H_5)_3SiH$.

An apparently new modification in this paper uses gradual addition of a halide of a transitional element to an excess of $(C_2H_5)_2SiH_2$ in the preparation of $(C_2H_5)_2SiHCl$ and $(C_2H_5)_2SiHBr$. This modification is under study in the continuing investigation of alkylhalosilanes with Si–H bonding.

Other investigators of alkylsilanes with Si–H bonding report a number of preparative methods. Partial reaction of $SiHCl_3$ with the Grignard reagent furnishes intermediates[3] $SiHCl_3 + C_2H_5MgBr \rightarrow C_2H_5SiHCl_2 + (C_2H_5)_2SiHCl$. Aluminum chloride catalyst allows numerous reactions such as: $(C_2H_5)_3SiSH + (C_2H_5)_2SiCl_2 \rightarrow (C_2H_5)_3SiCl + (C_2H_5)_2SiHCl + (C_2H_5)_2SiH_2$,[4] also $(C_2H_5)_3SiH + n\text{-}C_6H_{13}Cl \rightarrow (C_2H_5)_3SiCl + n\text{-}C_6H_{14}$,[4] and also $C_2H_5SiHCl_2 \rightarrow C_2H_5SiH_2Cl + C_2H_5SiCl_3$.[5]

Experimental Results

Table I lists 24 reactions of $(C_2H_5)_3SiH$ with halides or sulfates of 10 transitional elements and 5 elements in regular groups, or with sulfuric, nitric or chlorosulfonic acids. A median yield of 81% in Table I is based on the starting material present in the lesser amount as before.[2] When both $(C_2H_5)_3SiOH$ and $(C_2H_5)_3SiOSi(C_2H_5)_3$ are among the products calculations of yield in Table I exclude the minor organosilicon product. Direct conversion of a trialkylsilane to a hexaalkyldisiloxane occurs in the one-step reaction of triethylsilane and $HgSO_4$; this appears promising as a special method with trialkylsilanes.

Gradual addition of a deficiency of AgCl, $HgCl_2$ or $CuCl_2$ to excess $(C_2H_5)_2SiH_2$ gives favorable yields of $(C_2H_5)_2SiHCl$; similarly $HgBr_2$ and excess $(C_2H_5)_2SiH_2$ furnish new $(C_2H_5)_2SiHBr$. This general procedure seems to offer considerable promise in the preparation of alkylchlorosilanes or alkylbromosilanes with Si–H bonding.

Reaction of $(C_2H_5)_2SiH_2$ with a deficiency of iodine yields new $(C_2H_5)_2SiHI$, hydrolysis of which furnishes new $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$.

Discussion

Three different explanations for the reactions of $(C_2H_5)_3SiH$, $(C_2H_5)_3GeH$[1] and $(C_2H_5)_3SnH$[2] appear possible: heats of formation or free energies per equivalent of available halogen or oxygen in the compounds, also the appropriate ionization potentials of the elements, also, although they are definitely *not exactly comparable* and the value for silicon seems doubtful, oxidation potentials in aqueous solution. In the case of silicon the oxidation potential for Si(0) to Si(IV) is sufficiently questionable to eliminate any emphasis on it as a criterion.

Differences in bonding may have some importance. Triethylsilane reacts with $PtCl_4$ but not with K_2PtCl_6; $(C_2H_5)_3SiH$ reacts with 100% H_2SO_4 or HSO_3Cl but not with $C_6H_5SO_3Cl$. Triethylsilane does not react with powdered $KMnO_4$.

In keeping with available heats of formation or free energies, silicon has a strong preference for fluorine, oxygen or chlorine and a weaker preference for bromine or iodine. Triethylsilane and AgF yield a mixture containing at least $(C_2H_5)_3SiF$ and $(C_2H_5)_2SiF_2$.

Reactivity increases progressively from $(C_2H_5)_3SiH$ to $(C_2H_5)_3GeH$ to $(C_2H_5)_3SnH$ in reactions with halides of transitional elements or elements in regular groups. The *weak* acid CH_3COOH reacts

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[1] H. H. Anderson, THIS JOURNAL, **79**, 326 (1957).

[2] H. H. Anderson, *ibid.*, **79**, 4913 (1957).

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[5] B. N. Dolgov and others, *J. Gen. Chem.* (*USSR*), **27**, 710 (1957).