AN ISOTOPIC STUDY OF
THE HYDROLYSIS OF TRIPHENYLSILANE

by

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An Isotopic Study of the Hydrolysis of Triphenylsilane

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Summary.

The hydrolysis of triphenylsilane was carried out under conditions such that the reaction could be represented by the following equation

$$OH^{-} + (C_6H_5)_3SiH + C_5H_{10}NH \longrightarrow (C_6H_5)_3SiOH + H_2 + C_5H_{10}N^{-}$$

This reaction was investigated with respect to the isotope effects produced in the breaking of the silicon-hydrogen bond in the triphenylsilane and the nitrogen-hydrogen bond in the piperidine when the hydrogen in these bonds was replaced with deuterium.

The ratio of the rates of hydrolysis (k_D/k_H) of triphenylsilane-d and triphenylsilane, that is the ratio of the rates of breaking of the silicon-deuterium bond and the silicon-hydrogen bond was determined by competitive as well as kinetic methods. The results from both methods were in excellent agreement, giving values for k_D/k_H equal to 0.68 and 0.71 for the competitive and kinetic methods respectively. The ratio of the rates of breaking of the nitrogen-deuterium bond in piperidine-d and the nitrogen-hydrogen bond in piperidine was found to be 0.13 by the competitive method.

The large difference in the two isotope effects observed in the breaking of the silicon-hydrogen and the nitrogen-hydrogen bond for this hydrolysis, was taken to support a two step mechanism rather than a concerted process.

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INTRODUCTION

The hydrolysis of tri-substituted silanes has been investigated kinetically by F. P. Price and G. E. Dunn (22,7). The reaction was found to proceed according to the following equation,

$$OH^- + R_3SiH \xrightarrow{\text{proton donor}} R_3SiOH + H_2.$$

The attack of the hydroxyl group caused the displacement of the silane hydrogen with the pair of electrons which had constituted the bond. This hydrogen because of its reactivity would extract a proton from whatever chemical species that was present when the displacement occurred. The proton was usually obtained from the substance that was present in excess.

Kinetic evidence obtained by Dunn suggested that the nucleophilic attack was the slower step, that is, the breaking of the silicon-hydrogen bond was not involved in the rate-determining process. To determine if this was the case, the rates of hydrolysis of triphenylsilane and triphenylsilane-d were compared. The results of the independent kinetic runs showed that triphenylsilane-d reacted nearly six times faster than its protium analog (12).

In view of the fact that this result showed an abnormal isotope effect it has been the purpose of the present investigation to repeat the work employing competitive runs. Employing competitive runs eliminated the possibility of errors caused by impurities contaminating either of the silanes used. The runs were carried to approximately 50% completion. The gas evolved was oxidized to water, which was then purified and the deuterium content determined from its density, which was measured by the gradient density tube method (1). The rate ratio was calculated from the percent deuterium present in the water sample. In conjunction with these, independent kinetic runs were carried out as a secondary check on the rate ratio.

In addition to this work, the hydrolysis of triphenylsilane was carried out in a piperidine-deuterium oxide[1] solution to determine if this had any effect on the rate of formation of hydrogen.

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[1] The deuterium oxide having a mass spectrometric analysis of 99.73 atom percent deuterium was obtained through the Commercial Products Division of Atomic Energy of Canada, Ltd.

HISTORICAL

Isotopes in Chemical Reactions.

The employment of isotopes provides a comparatively new approach to the study of chemical reactions. Isotopes can be employed for this purpose in a dual role. In the first place they provide a method of tracing the route of a chosen atom in going from reactants to products. An outstanding example of this use is seen in the study of the hydrolysis of esters. If the ester is hydrolyzed in an acidic aqueous medium which has been enriched with the isotope O^{18}, the O^{18} is found to be in the alcoholic fraction (19,21); whereas the hydrolysis when carried out in an alkaline medium places the O^{18} in the acid fraction (4). In the second place, isotopes provide assistance in the investigation of the mechanism by which a reaction proceeds. It was with this latter use of isotopes that the present investigation is concerned.

In general, organic reactions are complex and do not proceed by any one simple process to give the products. The reactions usually consist of a series of steps, the slowest step governing the overall rate of reaction. Consider the following hypothetical reactions in which,

$$A \neq B \xrightleftharpoons[k_{-1}]{k_1} C \qquad (a)$$

and

$$C \neq D \xrightarrow{k_2} E \qquad (b)$$

where k_1 = the rate constant for the formation of C;

k_{-1} = the rate constant for the reverse reaction of C to give A and B;

and k_2 = the rate constant for the formation of E from C and D.

If k_1 is large compared to k_{-1} and k_2, that is, the formation of the intermediate C is nearly complete before any amount of E is formed, then the formation of E will be governed by the rate of reaction of C and D. On the other hand if k_2 is large compared to k_{-1} then as the intermediate C is formed it will react immediately with D to give the product E. The overall rate of reaction in this case will be governed by k_1. Finally if the two steps proceed at approximately the same rate then the overall rate of reaction will be dependent on the rates of both the involved steps.

The transition-state theory of Eyring (8) provides a theoretical basis of calculating the rate constant of the individual steps of a chemical reaction. This theory postulates that the reactants on becoming activated by the reaction process pass through an energy maximum before proceeding to the products. The energy maximum is termed the transition state or the activated complex but cannot be realized as an individual chemical species. The rate of reaction is simply the number of these activated complexes that pass over this energy barrier per unit time. Consider a simple bimolecular reaction

$$A + B \xrightleftharpoons{K^{\#}} [AB]^{\#} \longrightarrow \text{products}$$

where $[AB]^{\#}$ is the activated complex and $K^{\#}$ is the equilibrium constant for the reactants and the complex. The rate expression is

$$-\frac{d[A]}{dt} = k_2 [A][B] \qquad (a)$$

where k_2 = the rate constant for the bimolecular reaction;

$[A]$ = the concentration of the reactant A;

$[B]$ = the concentration of the reactant B.

Eyring, using a rigorous argument involving the activated complex $[AB]^{\#}$, showed that the theoretical rate expression was

$$-\frac{d[A]}{dt} = K^{\#} [A][B] \frac{kT}{h} \qquad (b)$$

where k = Boltzmann's constant; T = temperature of the reaction; h = Planck's constant; and $K^{\#}$ = the equilibrium constant for the reactants and the activated complex in the equation on page 4

$$K^{\#} = \frac{[AB]^{\#}}{[A][B]} .$$

By equating the equations (a) and (b) the rate constant for the reaction can be expressed as

$$k_2 = K^{\#} \frac{kT}{h} .$$

An additional factor, the transmission coefficient κ, which is the fraction of the activated complexes that actually decompose to give the products, must be added. Further substituting the statistical expression for $K^{\#}$, the complex equilibrium constant, gives the rate constant the following form

$$k_2 = \kappa \frac{kT}{h} \frac{f^{\#}}{f_a f_b} e^{-\Delta E_o/RT}$$

where $f^{\#}$ = partition function for the transition state;

f_a = partition function for the reactant A;

f_b = partition function for the reactant B;

and ΔE_o = the difference in the zero point energies between the activated complex and the reactants. This enables rate constants to be calculated on a theoretical basis providing that the partition function for the transition state could be evaluated.

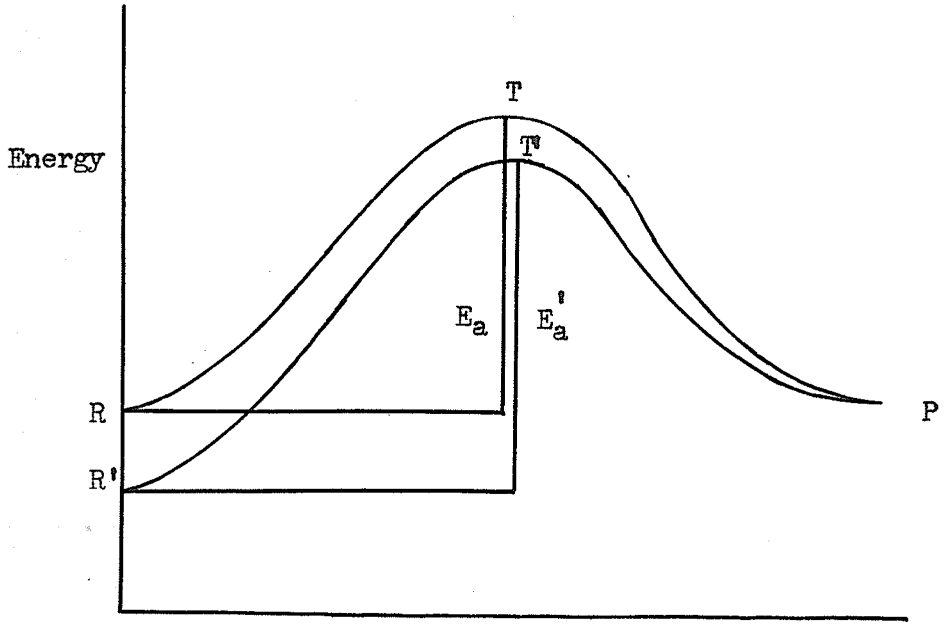
The absolute rate theory of Eyring provided a starting point for a theoretical calculation of the relative ratio of reaction rates of isotopic forms. This theory of isotope effects was developed by Bigeleisen (2,3) using only the vibrational frequencies of the atom being displaced. A rigorous argument by Eyring (9) shows that only these frequencies are involved in the reaction rate.

The absolute reaction rate theory shows the dependence of the rate constant on the zero point energy difference between the activated complex and the reactants. The energy of a bond is a function of the vibrational frequency, thus

$$E = (n + \tfrac{1}{2})\ h\ v \qquad \text{where } v = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{and } m = \frac{m_1 m_2}{m_1 + m_2}$$

E = energy of the bond; h = Planck's constant; v = vibrational frequency; n = quantum state of the molecule; k = restoring force and is a constant for a given chemical species; m = reduced mass of the atoms involved in the bond and m_1 and m_2 are the masses of the two concerned atoms. For zero point energy consideration, the lowest quantum state is necessary, for which n = 0. These relations show that if the reduced mass is increased the vibrational frequency and hence zero point energy is decreased. The passage of the reactants to the transition state causes a general loosening of bonds at the point of attack resulting in a decrease in vibrational frequency and zero point energy.

The introduction of a heavy isotope into a molecule should cause the reaction to proceed at a slower rate if the isotopically substituted bond is involved in the rate process. Both isotopic forms would react at equal rates if the position is not pertinent to the rate mechanism. The slower rate of reaction of the heavier isotopic form can best be explained with the aid of the following diagram.



Decomposition Chord.

where R = the normal reactant; R' = the isotopically substituted form;

T and T' = the corresponding transition states;

E_a and $E_{a'}$ = the corresponding activation energies of the two forms;

and P = products.

The heavy isotopic form because of its greater mass would have a lower vibrational frequency and hence a lower zero point energy in the ground state. The passage to the transition state will cause a decrease in zero point energy for both isotopic forms, but because the zero point energy of the heavier form is smaller than that for the light this decrease will be less for the heavy than for the normal form, resulting in a smaller difference in zero point energies in the activated state than in the ground state. The activation energy will be larger for the heavier form and therefore it should react at a slower rate. The above argument is general when bond breaking is concerned while a reversal of this argument holds when bond-formation is involved in the rate mechanism.

If in the above hypothetical reaction (page 3) the compound B has one of its bonds broken in the formation of the intermediate C then the use of isotopes can determine which of the two processes is rate controlling. This can be accomplished by preparing B with one of the atoms in the bond substituted with a heavier isotope. The rate of reaction of this compound will be less than that of the corresponding normal form if the overall rate is governed by the rate constant k_1. However the reactions will proceed at approximately equal rates if the rate is dependent only on the rate constant k_2.

The magnitude of the isotope effect will be determined by the relative increase in the reduced mass due to the introduction of the isotope (2,3). Considering a carbon-carbon bond the introduction of C^{14} will increase the reduced mass by approximately 8% whereas the introduction of deuterium in a carbon-hydrogen bond produces an increase of 85% and tritium produces an even greater increase of 160%. Many investigations have been carried out using various isotopes in this role, however only those in which the isotopes of hydrogen were employed will be discussed in the following examples.

The kinetics of the oxidation of isopropyl alcohol to acetone as determined by Westheimer and Novick (26) proceeded according to the following rate expression,

$$\frac{d\left[(CH_3)_2CO\right]}{dt} = k\left[CH_3CH(OH)CH_3\right]\left[HCrO_4^-\right]\left[H^+\right]^2$$

The kinetics observed, however, did not completely elucidate the mechanism. The position of attack was doubtful in that it could occur at the secondary hydrogen, the hydroxyl hydrogen, or elsewhere. This could however be answered by studying the rate of oxidation of 2-deutero propanol -2 which was undertaken by Westheimer and Nicolaides (27). Acetone was reduced catalytically with D_2 to the deuterated isopropyl alcohol $CH_3CD(OD)CH_3$ which was allowed to equilibrate with water to give a 55% yield of $CH_3DC(OH)CH_3$. The rate of oxidation of the deuterated compound was found to be 1/6 that of the rate of the normal compound. This conclusively proved that the removal of the secondary hydrogen atom was involved in the rate controlling process.

In the nitration of the benzene nucleus, kinetic data led Gillespie, Hughes and Ingold (10) to the conclusion that the removal of hydrogen from the benzene ring as a proton was not involved in the rate-determining step. Melander carried out a series of isotopic experiments on the nitration of benzene, toluene, bromobenzene and naphthalene, as well as the dinitration of toluene using tritium as a tracer to show that Gillespie, Hughes and Ingold were right (20). Melander introduced tritium into the ortho, meta, and para positions of toluene, thus preparing three types of tritium-containing toluenes. Normal toluene was nitrated with the nitrating agent consisting of 1:2 ratio of nitric and sulphuric acids that was tritium active. The analysis showed that no exchange of tritium had occurred during the nitration of the normal toluene.

It was supposed that on nitration toluene-4-t would lose all of its tritium, toluene-3-t would lose none, while toluene-2-t would lose the amount corresponding to the relative velocity of nitration of the two ortho positions having tritium and hydrogen. The dinitration of toluene proceeds to give 2,4, dinitrotoluene. The products were combusted to water which on analysis showed that the toluene-4-t had 2.2% tritium, toluene-3-t showed 99.0%, while two trials of toluene-2-t showed 51.9 and 49.7%. This indicated that tritium and hydrogen were displaced from the ortho position of toluene at equal rates and therefore the breaking of the carbon-hydrogen bond was not involved in the rate determining step.

This work was repeated by Lauer and Noland (18) using deuterated benzene for the nitration. The results of this investigation confirmed Melander's findings.

As a final example, Hughes, Ingold and co-workers (6) had proposed that the bimolecular elimination reaction (E2) proceeds by a rate-determining attack of the base on a β-situated hydrogen while the electronegative group X separates simultaneously with its bonding electrons.

$$Y: \; + \; HCR_2 — CR_2 — X \longrightarrow YH^+ \; + \; CR_2 = CR_2 + X^-$$

Kinetic evidence obtained on this type of reaction was easily explained by the proposed mechanism.

An isotopic study of this reaction was undertaken by V. J. Shiner (23) using α and β-deuterium substituted isopropyl bromide. According to this mechanism the β-substituted form should react at a slower rate whereas the α-substituted form should react at essentially the same rate as the normal form.

The β-substituted form was prepared by exchanging acetone with several deuterium oxide samples, followed by reduction of the acetone-$\underline{d}_6$ to isopropyl alcohol. The alcohol was then converted to the bromide. The α-form was prepared by reduction of acetone with lithium aluminum deuteride. The overall reaction was followed by titrating the Br^- ion as it was formed and the elimination reaction was determined from the final analysis. The results showed that in the β-substituted case the protium compound eliminated 6.7 times faster than the deutero-compound while the α-form reacted at essentially the same rate. This was in complete accord with the proposed mechanism of Hughes, Ingold and co-workers.

Hydrolysis of Silanes.

The hydrolysis of trialkylsilanes was first studied kinetically by Price (22). This investigation was carried out to determine the effect of alkyl substituents on the alkaline cleavage of the silicon-hydrogen bond. The cleavage was accomplished with potassium hydroxide in aqueous alcohol and could proceed by the following stoichiometric equations

$$OH^- + R_3SiH + R'OH \longrightarrow R_3SiOH + OR'^- + H_2 \qquad (a)$$

or

$$R_3SiH + OR'^- \longrightarrow R_3SiO^- + HR' \qquad (b)$$

where R and R' are alkyl groups.

According to equation (a) one of the products would be hydrogen gas whereas by equation (b) the hydrocarbon of the corresponding alcohol used in the hydrolyzing solution would be produced.

The actual product obtained in the gaseous state was determined by carrying out a series of hydrolyses employing various reagents and analyzing the evolved gas. In all cases the gas was shown to be at least 98% hydrogen indicating the reaction proceeds according to equation (a).

The hydrolysis of diethylmethylsilane was chosen for a study of the kinetics. To insure a smooth evolution of gas it was found necessary to shake the reaction vessel. The results of these hydrolyses indicated that the reaction was first order with respect to the silane and the hydroxyl ion. The reaction was shown to be dependent on the water concentration if water was present in the reaction solution. If the reaction was carried out under anhydrous conditions the reaction still proceeded; however in this case the proton was obtained from the alcohol used as solvent medium. This was explained by the following form of the rate constant

$$k = a \neq b(H_2O)$$

where k = the rate constant; a = the constant for the reactants present in anhydrous reactions; and b = the constant for the water dependence of the reaction.

The hydrolysis followed pseudo-first order kinetics to approximately 80% completion when all the reactants but silane were present in excess. The variation of the substituent groups showed that as the size and complexity increased, the rate constant decreased. This behavior was in accordance with the results obtained in nucleophilic displacement reactions in carbon chemistry.

A kinetic investigation of the mechanism of triarylsilane hydrolysis was carried out by G. E. Dunn (7). It was found that using Price's method, the hydrolysis with aqueous alkaline alcohol proceeded too rapidly for a kinetic study but the reaction did proceed at a convenient rate when the weaker base piperidine was employed (16). The reaction was found to be pseudo-first order in silane to approximately 80% completion when water was present in a twenty-fold excess and piperidine was employed as the solvent.

The effect of varying the water concentration in the reaction medium showed that the hydrolysis was half order in water up to concentrations of 2 molar. The order in water then began to increase with higher concentrations of water. The half order in water concentration was explained by the following relations. Price had previously shown that the reaction was first order in both silane and the hydroxyl ion. Therefore the disappearance of silane can be expressed as

$$\frac{-d\,[SH]}{dt} = k\,[SH][OH^-]$$

where SH represents silane.

The hydrolyzing solution equilibrated according to the following equation

$$PH + H_2O \overset{K}{\rightleftharpoons} PH_2^+ + OH^-$$

where PH represents piperidine,

and then $K = \frac{[PH_2^+][OH^-]}{[PH][H_2O]}$

Since $[PH_2^+] = [OH^-]$ the equilibrium can be rewritten as

$$K = \frac{[OH^-]^2}{[PH][H_2O]}$$

and therefore

$$[OH^-] = K^{\frac{1}{2}}\,[PH]^{\frac{1}{2}}\,[H_2O]^{\frac{1}{2}}$$

Substituting this value of the hydroxyl ion in the rate expression

$$\frac{-d\,[SH]}{dt} = kK^{\frac{1}{2}}\,[SH][PH]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}$$

This accounted for the observed half order in water but not the increasing order in water concentrations higher than 2 molar. To account for this effect the following argument was put forward. The production of hydrogen gas as one of the products indicated that when the silane hydrogen with its pair of electrons is displaced it picks up a proton from one of the reactants. At low water concentrations the proton evidently came from the piperidine which was far in excess of the water concentration, thus

$$OH^- + SH + PH \longrightarrow SOH + H_2 + P^-$$

The rate expression then became

$$\frac{-d\,[SH]}{dt} = kK^{\frac{1}{2}}\,[SH]\,[H_2O]^{\frac{1}{2}}\,[PH]^{3/2}$$

A proton should be more easily obtained from the water and as the water concentration increases this apparently happened, thus increasing the order in water,

$$OH^- + SH + H_2O \longrightarrow SOH + H_2 + OH^-$$

The rate expression then became

$$\frac{-d\,[SH]}{dt} = k\,K^{\frac{1}{2}}\,[SH]\,[PH]^{\frac{1}{2}}\,[H_2O]^{3/2}$$

The three-halves order in water was not realized because at higher water concentrations the reaction solution did not remain homogeneous, separating into two distinct layers.

In order to confirm this interpretation an attempt was made to find the order of all the reactants in a single medium. Methyl cellosolve was chosen as the solvent for this experiment. The results of this portion of the work showed that the reaction was half order in piperidine, but zero order in water at low water concentrations. The zero order in water at low concentrations was taken to show that methyl cellosolve replaced water in the preliminary equilibrium with piperidine

$$CH_3OCH_2CH_2OH + PH \rightleftharpoons CH_3OCH_2CH_2O^- + PH_2^+$$

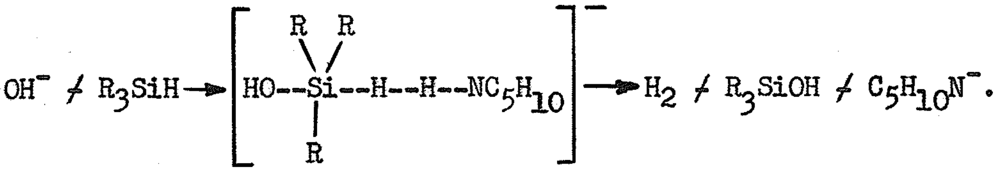
If this were true then the attacking species would be the 2-methoxyethoxy ion instead of the hydroxyl ion. This was verified by carrying out a larger scale hydrolysis using .2% water solution. A 78% yield of triphenyl-(2-methoxyethoxy)-silane was obtained.

All the evidence thus far obtained indicated that the reaction was extremely selective with respect to the nucleophilic reagents present in the reacting solution. For example, when the hydrolysis was carried out with wet piperidine, the attacking species was the hydroxyl ion even though the nucleophilic reagents, piperidine, and water were also present. The selection apparently tends toward the most nucleophilic reagent present. This was further substantiated when the reaction was carried out in methyl cellosolve, here the attacking species was found to be the 2-methoxyethoxy ion which is a stronger nucleophilic reagent than the hydroxyl ion. On the other hand there appeared to be little or no selectivity for the proton donor in the formation of hydrogen. The proton apparently is obtained from the reagent present in excess.

This evidence suggested that the attack of the nucleophilic reagent was the slow step. That is, the displacement of the hydrogen was not involved in the rate controlling process. For a verification of this, triphenylsilane-d was prepared and its rate of hydrolysis checked against that of the normal silane. The ratio of the independent rates of hydrolysis showed that the triphenylsilane-d reacted almost six times faster than its protium analog (12).

This showed that contrary to the above suggestion, the breaking of the silicon-hydrogen bond is part of the rate controlling process. However, the sign of the isotope effect is opposite to that expected on the basis of the previous discussion. This was interpreted in the following manner. It is conceivable that some reactions which involve breaking bonds to atoms of different masses will not show any considerable isotope effect because of a fortuitous similarity of zero-point energies of the transition and resting states of the reactants.

While the lack of a detailed knowledge of the configuration of the transition state for the hydrolysis of triphenylsilane does not permit a complete interpretation of the observed results, it seems likely that the abnormal effect should be attributed in large part to the fact that the reaction effectively involves the displacement of a hydride ion. Because of the rather low electron affinity of hydrogen atoms [17 kcal. per mole (13)] such a displacement would not be expected to occur at ordinary temperatures unless the hydrogen is continuously bound to some other atom or atoms throughout the course of the reaction. This means that if the old bond has been largely destroyed in the transition state, the new bond (hydrogen-hydrogen) must have already attained considerable strength. The transition state for the hydrolysis would then be represented as is shown in the overall equation



$$OH^- \neq R_3SiH \rightarrow \left[HO\text{--}\underset{R}{\overset{R\ \ R}{Si}}\text{--}H\text{--}H\text{--}NC_5H_{10} \right]^- \rightarrow H_2 \neq R_3SiOH \neq C_5H_{10}N^-.$$

Since the hydrogen-hydrogen bond has a rather large stretching force constant $\left[5.76 \times 10^5 \text{ dynes per cm. } (14)\right]$ the restoring force for vibrational displacement of the hydrogen atom may well be larger in the transition state than in the silane. Reversal of the argument outlined above for the normal isotope effect would then account for the abnormal effect observed in this reaction.

Several reactions in which hydrogen gas was formed by the displacement of the supposed hydride ion were investigated by K. E. Wilzbach and L. Kaplan (28). In these hydrolyses tritium was employed in place of deuterium to enhance any isotope effect. Price's alkaline alcoholic hydrolysis of tripropylsilane was repeated and it was found that the relative ratio of hydrolysis (ratio of k_T/k_H) was 0.7. The results of the hydrolysis of lithium aluminum hydride and lithium borohydride were inconsistent falling in the range of 1.2 to 0.8 (29, 30).

The hydrolysis of triphenylsilane was carried out using a piperidine-water solution in which the water was one molar. The runs were carried to 40% completion employing competitive hydrolysis. During the reaction portions of the evolved gas were isolated by cooling the reaction apparatus to -80°C. Tritium analyses were carried out on these gas volumes using an ion chamber and a vibrating reed electrometer. The ratio of k_T/k_H was found to be 0.79. This value was in good agreement with the theoretical value of 0.8 which was calculated by Bigeleisen's method considering only the stretching frequencies of the silicon-hydrogen and the hydrogen-hydrogen bonds (2,3,9). The theoretical ratio of k_D/k_H was calculated to be 0.9 when deuterium is used in place of tritium in this hydrolysis.

These results were clearly incompatible with those of Gilman, Dunn and Hammond who found that triphenylsilane-d reacted nearly six times faster than triphenylsilane (12), hence it was part of the present investigation to clear up the discrepancy.

EXPERIMENTAL

According to the kinetic evidence obtained by Dunn (page 13), the hydrolysis of triphenylsilane in moist piperidine proceeds according to the equation below, provided the water concentration is not much greater than 2 molar

$$OH^- + R_3SiH + C_5H_{10}NH \longrightarrow R_3SiOH + H_2 + C_5H_{10}N^-$$

From this equation it can be seen that two bonds are broken in the formation of hydrogen gas. These are the silicon-hydrogen bond in triphenylsilane and the nitrogen-hydrogen bond in the piperidine. It was the purpose of the present research to investigate the isotope effect produced by substituting deuterium for the hydrogen in each of these bonds.

The relative rates of silicon-hydrogen and silicon-deuterium bond breaking were measured by allowing triphenylsilane and triphenylsilane-_d_ to compete for protons in piperidine containing about 2 mole/l. of water, then determining the fraction of deuterium in the gas produced in an incomplete hydrolysis. The relative rates of nitrogen-hydrogen and nitrogen-deuterium bond breaking were measured in a similar way by analyzing the hydrogen produced when triphenylsilane is hydrolyzed in an excess of piperidine and piperidine-_d_.

The ratio of the rates of breaking of the silicon-hydrogen and silicon-deuterium bonds was also determined by a comparison of the rate constants obtained from independent pseudo-first order kinetic hydrolysis of triphenylsilane and triphenylsilane-_d_. This served as a check on the rate ratio obtained from the corresponding competitive hydrolysis.

All these experimental procedures will be described under three main headings, which are:

(1). Materials

(2). Kinetic Runs

(3). Competitive Runs.

Materials.

Anhydrous Ether. Triphenylchlorosilane is readily hydrolyzed by water; therefore, the ether used as refluxing medium in the preparation of triphenylsilane had to be thoroughly dried. The ether was dried over sodium wire, distilled, and allowed to stand over calcium hydride until required.

Mercury. The silane hydrolyses were carried out in a gas buret over mercury. Mercury was also employed in the transfer and dilution burets in which the hydrogen was contained. This choice rested on the low solubility of hydrogen gas in mercury. The mercury was purified by two filtrations into dilute nitric acid. These were followed by several washings with distilled water and finally a vacuum distillation. After each run the mercury was refiltered, washed and dried.

Piperidine. Employed as the weak base in silane hydrolysis, the piperidine was purified by distillation through a fifteen-plate fractionating column. The fraction boiling at 106°C. (740 mm.) was collected.

Toluene. Toluene was used as the solvent for the silanes in the hydrolyses, as well as in the thermostat temperature regulator. Purification consisted of four stirrings with concentrated sulphuric acid to remove impurities in the form of sulphur-containing compounds.

The toluene was then washed with sodium carbonate, followed by several washings with distilled water. It was dried over anhydrous sodium sulphate and distilled through a fifteen-plate column. The fraction boiling at 110.5°C. (740 mm.) was collected.

Bromobenzene. Used in the gradient density tube, the bromobenzene was distilled through the same fractionating column, collecting the fraction boiling at 155°C. (740 mm.).

Kerosene. Kerosene was the second component in the gradient density tube solutions. Commercial kerosene in 500 ml. portions was stirred with concentrated sulphuric acid to remove olefins and sulphur compounds. Each portion was subjected to four such treatments. It was then washed with sodium carbonate, followed by several washings with distilled water. It was dried over anhydrous sodium sulphate and finally distilled. The fraction boiling in the range of 190-220°C. (740 mm.) was collected and found to have a specific gravity of 0.788 as measured by a hydrometer at room temperature. To check for freedom from unsaturates the kerosene was tested with bromine water and potassium permanganate. After several hours standing there was no noticeable decolorization of either of the reagents used.

Preparation of the Kerosene-bromobenzene Solutions. The kerosene and bromobenzene were mixed to give two solutions having densities of 0.99 and 1.02 as measured by a hydrometer at room temperature.

Preparation of Standard Water-Deuterium Oxide Solutions. These solutions were employed as standards for determining the deuterium content of the unknown samples. The range of the density tube was from 0 to 10% deuterium oxide so that the standards were prepared to cover this range at 2% intervals. Serum vials with self-sealing rubber stoppers were used as containers. The vials were thoroughly cleaned with sulphuric acid-dichromate cleaning solution and rinsed with ammonium hydroxide followed by distilled water. They were then dried in an oven at 110°C. and stored in a desiccator.

The standards were prepared on a weight percent basis using water and deuterium oxide to give a total weight of 5 gm. The water was purified by an alkaline-permanganate distillation followed by three other distillations from an all Pyrex glass still. The deuterium oxide had a mass-spectrometric analysis of 99.73 atom-percent deuterium therefore, the weight of deuterium oxide used was adjusted accordingly. The deuterium oxide and the water were introduced with a hypodermic needle and syringe directly into the sealed serum vials through the stoppers. The weighings were carried out on an analytical balance. The solutions prepared are listed in the following table.

TABLE I

Standard Water-Deuterium Oxide Solutions.

Standard No.	Weight percent D_2O
1	0.000
2	1.995
3	3.899
4	5.984
5	7.979
6	9.975

<u>Preparation of Triphenylsilane.</u> The triphenylsilane was prepared by the reduction of the corresponding chlorosilane using lithium aluminum hydride as reducing agent (11). The reduction proceeded according to the following equation

$$4(C_6H_5)_3SiCl + LiAlH_4 \longrightarrow 4\ (C_6H_5)_3SiH + LiCl + AlCl_3.$$

Triphenylchlorosilane, 4.4 gm. (.015 mole) and lithium aluminum hydride, 0.57 gm. (.015 mole) were placed in 150 ml. of ether in a round-bottom flask. This suspension was refluxed for six hours under a dry atmosphere, after which the excess lithium aluminum hydride was hydrolyzed with water-saturated ether. When the violent reaction had subsided this was further treated with dilute hydrochloric acid. The ether layer was separated and dried with anhydrous sodium sulphate.

The ether was distilled, leaving a pale yellow oil contained in a 50 ml. distilling flask. The flask was filled with glass wool to prevent bumping, and the oil distilled under the reduced pressure of a water pump (9 cm.). The fraction boiling in the range of 204-6°C. was collected, which solidified on cooling to room temperature. Recrystallization from petroleum ether (boiling range 60-80°C.) yielded a small amount of crystalline material. Melting point determination (m.p. 144°C.) showed the filtered crystals to be triphenylsilanol. No pure triphenylsilane was obtained because of this co-distillation of triphenylsilanol. The oily material was then redistilled under lower pressure (2 mm.) to reduce co-distillation and the fraction boiling in the range of 165-168°C. was collected. After several recrystallizations from petroleum ether this material yielded 2.4 gm., of triphenylsilane (m.p. 44°C. uncorrected).

Since the supply of lithium aluminum deuteride[2] was limited, several preparations of triphenylsilane were carried out to find optimum conditions. In these runs, however, only the reflux period was altered, as it has been previously shown that a 3:1 mole ratio of triphenylchlorosilane to lithium aluminum hydride gave maximum yield (7). The results can best be summarized in the following table.

TABLE II

Effect of the Reflux Period on the Yields of Triphenylsilane

Preparation Number	Weight of Triphenylchlorosilane used (gm.)	Reflux Period (hr.)	Percent Yield
2	13.2	48	64
3	4.4	24	66
4	4.4	12	64
5	4.4	6	60
6[a]	4.4	6	60

[a] In this preparation the lithium aluminum hydride and the ether were refluxed for six hours before the triphenylchlorosilane was added.

This table indicated that down to the 12 hour reflux period no appreciable decrease in yield was observed. However the six hour preparations did show a decided decrease, so that the 12 hour period was selected for preparation of triphenylsilane-d.

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[2] The lithium aluminum deuteride, having a reported deuterium content of 96 atom percent, was obtained as a gift from Dr. E. W. R. Steacie of the National Research Council.

Preparation of Triphenylsilane-d. Triphenylchlorosilane, 10.4 gm. (.036 mole) and lithium aluminum deuteride, 0.5 gm. (.012 mole) were placed in 200 ml. of ether and the resulting suspension was refluxed for 12 hours. The excess lithium aluminum deuteride was hydrolyzed with water-saturated ether followed by dilute hydrochloric acid. The ether was distilled off and the oily residue distilled under reduced pressure (1 mm.). The fraction boiling in the range of 162-165°C. was collected. Recrystallization from petroleum ether yielded 4.3 gm. of triphenylsilane-d (m.p. 44°C. uncorrected). Mixed melting point determination with triphenylsilane showed no depression.

The triphenylsilane-d was analyzed for deuterium by a complete hydrolysis of a sample which proceeded according to the following equation

$$OH^- + (C_6H_5)_3SiD \xrightarrow{C_5H_{10}NH} (C_6H_5)_3SiOH + HD + C_5H_{10}N^-$$

The gas obtained from the hydrolysis was oxidized to water and the percent deuterium oxide determined from the density of the water sample. The procedure followed in this analysis will be described in later sections.

Analysis.

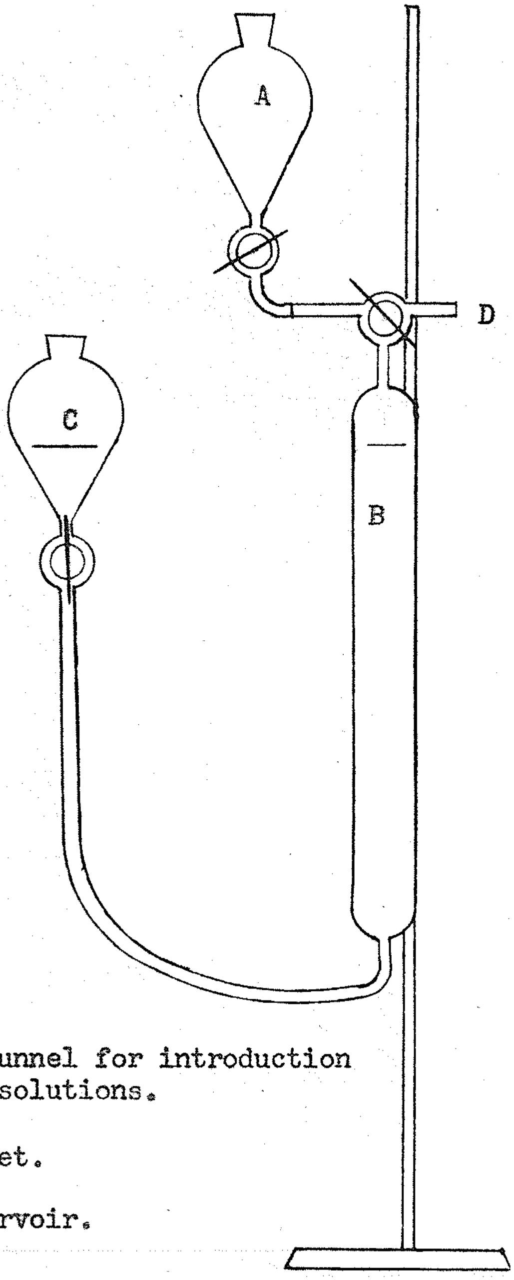
Weight of water sample	0.4347 gm.
Percent deuterium oxide	1.530
Weight of deuterium oxide in sample	0.006651 gm.
Moles of deuterium as HD $\frac{.006651 \times 2}{20} =$	0.0006651
Volume of gas obtained from the hydrolysis	18.10 ml.
Theoretical moles of HD from this volume $\frac{18.10 \times 739.4 \times 273}{22,414 \times 760 \times 296} =$	0.0007251
Atom percent deuterium in triphenylsilane-d $\frac{.0006651}{.0007251} \times 100 =$	91.8

Kinetic Runs.

Apparatus and Procedure. The apparatus used in the kinetic runs was arranged as shown in Fig. 1. The reactions were carried out in a 100 ml. gas buret over mercury. The buret was enclosed in a water jacket through which water from a thermostat was circulated. The thermostat was maintained at 25.000 ± .006°C. by means of a toluene-mercury finger regulator. To one end of the buret's three-way stopcock, a separatory funnel was attached for the purpose of introducing the reactants into the gas buret. The other end was left open, in order that a second buret could be attached for the transfer of hydrogen gas after the reaction had been completed.

It has been shown by Price that in order to obtain a smooth evolution of hydrogen the reaction vessel had to be shaken. A stirring motor fitted with an off-centered weight was attached to the ring stand holding the reaction buret for this purpose. The vibration produced by running the motor at moderate speed provided the necessary agitation. The voltage, and hence the amount of agitation, was controlled by means of a Vari-ac. The majority of the runs were carried out with this Vari-ac set at 35 volts.

All kinetic runs were carried out by the same procedure, which was as follows. The water circulating system was started a half hour previous to the commencement of the run, in order to bring the buret to the temperature of the thermostat. The sample of triphenylsilane (.00192 mole) was weighed out and introduced into the separatory funnel where it was dissolved in 10 ml. of toluene (.0937 mole) from



A - Separatory funnel for introduction of reactant solutions.

B - Reaction buret.

C - Mercury reservoir.

Fig. 1. Hydrolysis Apparatus.

a pipet. Into the resulting solution were pipetted 20 ml. of the hydrolyzing solution, consisting of piperidine (.203 mole) and water (.0551 mole) or deuterium oxide (.0552 mole). These two solutions were thoroughly mixed and the stopcock turned so that the separatory funnel was connected to the buret. The mercury level was lowered and the reactant solution drawn into the buret. The mercury level was now raised to exclude any air that was left in the buret, the stopcock closed and the stop-watch started. During the first few minutes the evolution of gas was extremely slow, resulting in a negligible loss of hydrogen during the introduction of the reactants into the buret.

The reaction was followed by recording the volume of hydrogen evolved during intervals of five minutes. The gas in the buret was maintained at atmospheric pressure by depressing the mercury reservoir as the reaction proceeded. The mercury level of both the reservoir and buret, including a correction for the weight of the reactant solution in the gas buret, was accurately maintained by means of a vertical cathetometer. The reaction was followed to approximately 50% completion. The hydrolyses were all carried out under conditions yielding pseudo-first order kinetics, the rate constants for the various runs were calculated from the slope of the line obtained by plotting log (a-x) versus the time in seconds. In the logarithm expression, a = calculated volume of gas that would be obtained from the complete hydrolysis, and x = volume of gas obtained at time t. The volume of gas evolved was first corrected for the presence of solvent vapors. This correction was obtained by passing the total gas produced at the end of a reaction through a Dry Ice trap three times and measuring the decrease in volume. The mean decrease for six runs was found to be 8.3%. The volume of gas collected at each time, t, during all the runs was corrected by this factor, assuming that the solvent vapors and hydrogen were present in a constant ratio.

TABLE III

Volume Decrease Due To Solvent Vapors

Run No.	Wet Volume (ml.)	Dried Volume (ml.)	Difference (ml.)	Percent Decrease
10	37.7	35.3	2.4	6.5
11	47.4	43.9	3.5	7.4
12	43.7	40.1	3.6	8.3
16	13.2	11.6	1.6	12.2
18	27.1	24.7	2.4	8.9
19	23.9	22.4	1.5	6.3
			Mean percent decrease	8.3

Preliminary Experiments. The points representing approximately the first six percent of the reaction at 25°C. did not fit the pseudo-first order plot[3], as can be seen in figures 2, 3, and 4. Attempts were therefore made to determine the cause of this initial lag which could possibly be due to; (a) inefficient mixing, (b) absorption of the evolved gas in the reaction solution, and (c) the presence of the solvent vapors in the gas phase.

That the lag was not due to inefficient mixing was proved by the following procedures. The two reactant solutions were introduced into the reaction buret without any stirring whatever and the reaction was followed kinetically. The reactants were next introduced into the separatory funnel and stirred thoroughly before being drawn into the reaction buret. Finally the silane solution, piperidine, and the water were introduced separately into the buret. In all these runs the initial lag remained, and was of approximately the same magnitude.

Further evidence was obtained by carrying out the hydrolyses under fixed conditions but altering only the amount of agitation of the reaction buret. This was accomplished by altering the voltage through the stirring motor by means of the Vari-ac. Reactions were carried out with the Vari-ac set at 35, 45, and 50 volts, which had no effect on the magnitude of the lag although increasing voltage did increase the rate constant. This effect can be illustrated with the rate constants listed in Table IV, page 33, where runs 1, 2, and

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[3] A similar behavior was observed by Dunn (7) although of lesser magnitude.

3 were carried out at 35 volts while run 4 was at 45 volts and runs 5 and 6 with the Vari-ac set at 50 volts. Because of this dependence of the rate on the amount of agitation subsequent runs were all carried out at the same Vari-ac setting (35 volts).

If the initial lag was due to the absorption of hydrogen in the reaction solution then the final volume of gas obtained from a completed hydrolysis should be considerably less than the theoretical volume. The completed runs however showed in all cases from 97 to 100% of the theoretical volume. Further, if the reaction was carried out at various temperatures the lag should exhibit a temperature dependence. The solubility of hydrogen would be greater and consequently the lag more pronounced at the lower temperature. Therefore runs were carried out at 0° and 10°C. The lag represented 6% of the reaction at 25°C; 1.4% of the reaction at 10°C; and 1% at 0°C. It is seen that this variation is in the wrong direction to be accounted for by hydrogen solubility.

The lag could be satisfactorily accounted for as due to the presence of solvent vapors in the gas. The evolution of hydrogen during the initial portion of the reaction, although proceeding according to first order kinetics, might be too fast to permit saturation with the solvent vapors. The concentration of solvent vapors would thus increase steadily as the hydrogen evolution slowed down until equilibrium conditions were attained. Since a constant percent correction for solvent vapors is applied (see p. 30) to each reading, pseudo-first order kinetics would not be observed until the equilibrium is attained. This interpretation is in agreement with the results of the runs carried out at 0° and 10°C. The solvent vapor pressure would be smaller and hence the equilibrium would be attained sooner at the lower temperatures.

Since this lag was constant and unavoidable, the points plotted during the first six percent of subsequent runs were not included in calculating slopes and rate constants.

TABLE IV

Rate Constants for the Preliminary Kinetic Runs.

Run No.	Reactants (Toluene used as Solvent)	Rate Constant x 10^4 sec^{-1}
1	R$_3$SiH in Solution 1	1.287 ± .045
2	R$_3$SiH in Solution 1	1.273 ± .077
3	R$_3$SiH in Solution 1	1.272 ± .080
4[a]	R$_3$SiH in Solution 1	1.516 ± .035
5[a]	R$_3$SiH in Solution 1	1.588 ± .040
6[a]	R$_3$SiH in Solution 1	1.584 ± .080
7	R$_3$SiH in Solution 1 at 0°C.	0.140 ± .004
8	R$_3$SiH in Solution 1 at 10°C.	0.217 ± .007

[a] Runs 4, 5 and 6 were carried out under different conditions of agitation. (see p. 32).

Solution 1 = 20 ml. of Piperidine (.203 mole) and water (.0551 mole).

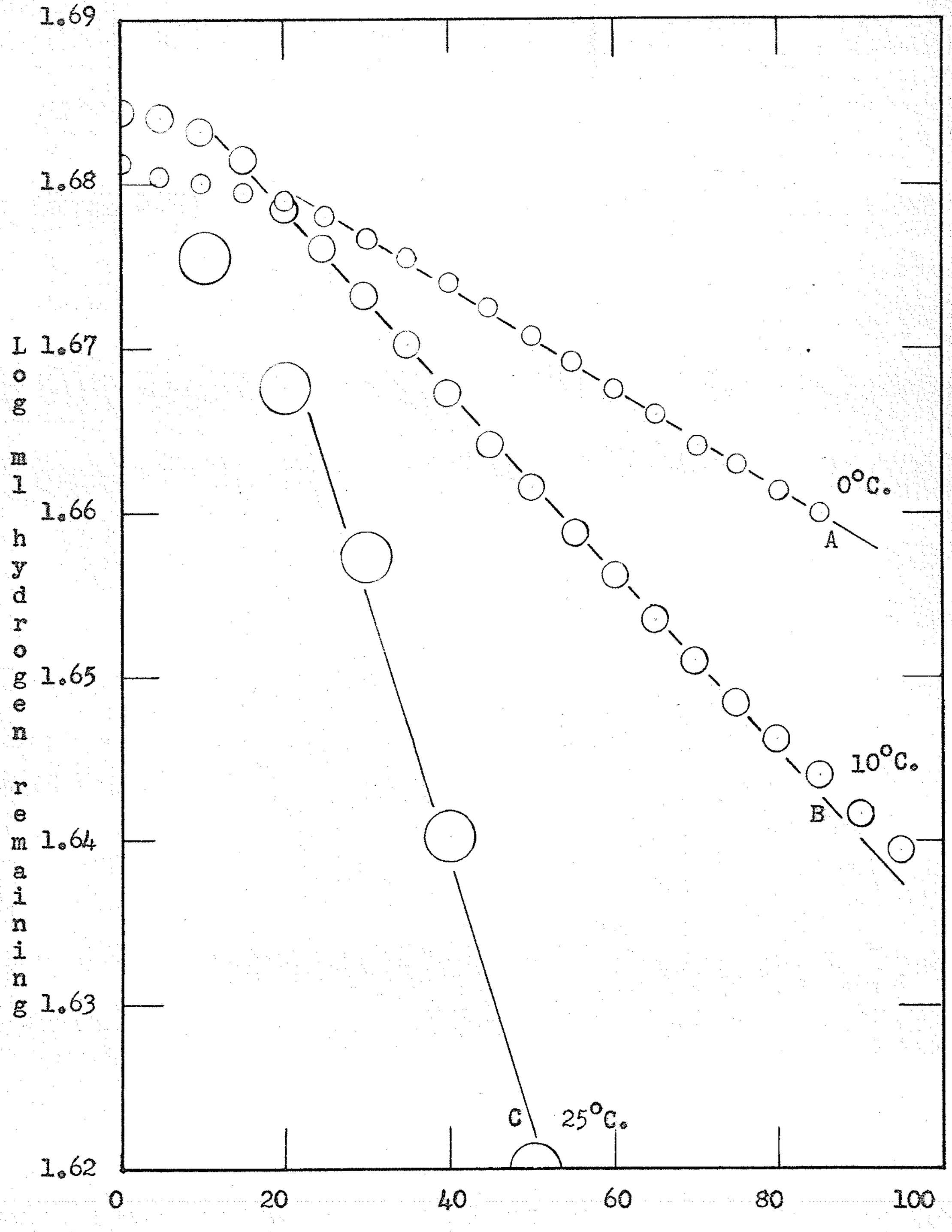


Fig. 2. Effect of Temperature on the rate of Hydrolysis of Triphenylsilane in Piperidine containing 2.75 mole of H_2O per Liter.

TABLE V

Run 1.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gms.; buret temperature = 25°; pressure = 738 mm.
Calculated volume of gas at this temperature and pressure = 48.38 ml.
x = corrected volume of gas evolved; a-x = hydrogen remaining.

Time Min.	Buret Readings (ml)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.38	1.6846
3	0.40	0.37	48.01	1.6813
6	0.60	0.55	47.83	1.6797
9	0.80	0.73	47.65	1.6781
12	1.00	0.92	47.46	1.6763
15	1.50	1.37	47.01	1.6722
18	2.40	2.20	46.18	1.6644
21	3.30	3.02	45.36	1.6567
24	4.10	3.76	44.62	1.6495
27	5.10	4.67	43.71	1.6406
30	6.00	5.50	42.88	1.6322
33	7.00	6.41	41.97	1.6229
36	8.00	7.33	41.05	1.6133
39	9.10	8.34	40.04	1.6025
42	10.20	9.34	39.04	1.5915
45	11.40	10.44	37.94	1.5791
48	12.60	11.54	36.84	1.5663
51	13.80	12.64	35.74	1.5532
54	14.70	13.42	34.96	1.5433
57	15.60	14.29	34.09	1.5326
60	16.70	15.30	33.08	1.5195
65	17.80	16.30	32.08	1.5062
70	19.20	17.59	30.79	1.4884
75	20.40	18.69	29.69	1.4726
80	21.50	19.69	28.69	1.4578
85	22.70	20.79	27.59	1.4407
90	23.70	21.71	26.67	1.4260
95	24.60	22.53	25.85	1.4125
100	25.70	23.54	24.84	1.3952
105	26.70	24.46	23.92	1.3788
110	27.60	25.28	23.10	1.3636

TABLE VI

Run 2.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25o.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 731.7 mm.
Calculated volume of gas at this temperature and pressure = 48.86 ml.
x = corrected volume of hydrogen evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.86	1.6889
5	0.60	0.55	48.31	1.6840
10	1.20	1.10	47.76	1.6790
15	2.40	2.20	46.66	1.6690
20	4.00	3.66	45.20	1.6551
25	5.70	5.22	43.64	1.6399
30	7.50	6.87	41.99	1.6231
35	9.40	8.61	40.25	1.6048
40	11.40	10.44	38.42	1.5845
45	13.50	12.47	36.39	1.5610
50	15.30	14.01	34.85	1.5422
55	16.30	14.93	33.93	1.5306
60	18.40	16.85	32.01	1.5051
65	19.60	17.95	30.91	1.4901
70	20.90	19.14	29.72	1.4731
75	22.10	20.24	28.62	1.4567
80	23.10	21.16	27.70	1.4425
85	24.20	22.17	26.69	1.4254
90	25.30	23.17	25.69	1.4097
95	26.40	24.18	24.68	1.3925
100	27.40	25.10	23.76	1.3748
105	28.30	25.92	22.94	1.3606
110	29.20	26.75	22.11	1.3446
115	30.10	27.57	21.29	1.3281
120	30.90	28.30	20.56	1.3131

TABLE VII

Run 3.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of Sample = 0.5000 gm.; buret temperature = 25°; pressure = 741.8 mm.
Calculated volume of gas at this temperature and pressure = 48.20 ml.
x = corrected volume of hydrogen evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.20	1.6830
5	0.30	0.27	47.93	1.6806
10	0.90	0.82	47.38	1.6756
15	1.70	1.56	46.64	1.6688
20	3.00	2.75	45.45	1.6576
25	4.90	4.49	43.71	1.6406
30	7.10	6.50	41.70	1.6201
35	9.20	8.43	39.77	1.5996
40	10.90	9.98	38.22	1.5823
45	12.70	11.63	36.57	1.5631
50	14.50	13.28	34.92	1.5431
55	16.20	14.84	33.36	1.5232
60	17.50	16.03	32.17	1.5074
65	18.50	16.95	31.25	1.4948
70	20.00	18.32	29.88	1.4746
75	21.20	19.42	28.78	1.4591
80	22.50	20.61	27.59	1.4407
85	23.70	21.71	26.49	1.4231
90	24.90	22.81	25.39	1.4046
95	25.90	23.72	24.48	1.3888
100	26.90	24.64	23.56	1.3722
105	27.80	25.46	22.74	1.3568
110	28.80	26.38	21.82	1.3391
115	29.60	27.11	21.09	1.3240
120	30.40	27.85	20.35	1.3087
125	31.10	28.49	19.71	1.2947

TABLE VIII

Run 4.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 746 mm.
Calculated volume of gas at this temperature and pressure = 47.92 ml.
x = corrected volume of hydrogen evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	47.92	1.6805
5	0.70	0.64	47.28	1.6746
10	1.70	1.56	46.36	1.6662
15	3.30	3.02	44.90	1.6522
20	5.30	4.85	43.07	1.6342
25	7.40	6.78	41.14	1.6142
30	9.60	8.79	39.13	1.5925
35	12.10	11.08	36.84	1.5663
40	13.90	12.73	35.19	1.5464
45	15.60	14.29	33.63	1.5267
50	17.30	15.85	32.07	1.5060
55	18.70	17.13	30.79	1.4884
60	20.10	18.41	29.51	1.4699
65	21.60	19.79	28.13	1.4492
70	23.00	21.07	26.85	1.4289
75	24.30	22.26	25.66	1.4092
80	25.60	23.45	24.47	1.3886
85	26.70	24.46	23.46	1.3703
90	27.80	25.46	22.46	1.3514
95	28.80	26.38	21.54	1.3332
100	29.80	27.30	20.62	1.3143
105	30.60	28.03	19.89	1.2987
110	31.50	28.85	19.07	1.2806

TABLE IX

Run 5.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 737.2 mm.
Calculated volume of gas at this temperature and pressure = 48.49 ml.
x = corrected volume of hydrogen evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.49	1.6856
5	0.50	0.46	48.03	1.6815
10	0.90	0.82	47.67	1.6782
15	2.00	1.83	46.66	1.6690
20	3.60	3.80	45.19	1.6551
25	5.70	5.22	43.29	1.6362
30	7.60	6.96	41.53	1.6183
35	9.70	8.89	39.60	1.5977
40	11.70	10.72	37.77	1.5773
45	13.80	12.64	35.85	1.5545
50	16.10	14.75	33.74	1.5281
55	18.10	16.58	31.91	1.5059
60	20.00	18.32	30.17	1.4796
65	21.60	19.79	28.70	1.4579
70	22.90	20.98	27.51	1.4395
75	24.20	22.17	26.32	1.4203
80	25.30	23.17	25.32	1.4034
85	26.60	24.37	24.12	1.3824
90	27.80	25.46	23.03	1.3623
95	28.90	26.47	22.02	1.3428
100	29.80	27.30	21.19	1.3261
105	30.70	28.12	20.37	1.3090
110	31.60	28.84	19.65	1.2934
115	32.60	29.86	18.63	1.2702
120	33.40	30.60	17.89	1.2502
125	34.20	31.88	16.61	1.2204

TABLE X

Run 6.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 743.2 mm.
Calculated volume of gas at this temperature and pressure = 47.92 ml.
x = corrected volume of hydrogen evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	47.92	1.6805
5	0.80	0.73	47.19	1.6738
10	2.60	2.38	45.54	1.6584
15	4.90	4.49	43.43	1.6378
20	7.30	6.69	41.23	1.6152
25	9.70	8.89	39.03	1.5914
30	11.60	10.63	37.29	1.5715
35	13.70	12.55	35.37	1.5487
40	15.70	14.38	33.54	1.5255
45	17.70	16.21	31.71	1.5012
50	19.50	17.86	30.06	1.4780
55	21.10	19.33	28.59	1.4562
60	22.80	20.88	27.04	1.4320
65	24.10	22.08	25.84	1.4123
70	25.30	23.17	24.75	1.3936
75	26.50	24.26	23.66	1.3740
80	27.70	25.37	22.55	1.3532
85	28.90	26.47	21.45	1.3314
90	30.00	27.48	20.44	1.3104
95	30.90	28.30	19.62	1.2927
100	31.90	29.22	18.70	1.2718
105	32.70	29.95	17.97	1.2546
110	33.60	30.78	17.14	1.2340
115	34.20	31.33	16.59	1.2199
120	34.80	31.88	16.04	1.2052
125	35.40	32.48	15.49	1.1900

TABLE XI

Run 7.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 0°.

Weight of sample = 0.5000 gm.; buret temperature = 0°; pressure = 741.4 mm.
Calculated volume of gas at this temperature and pressure = 48.24 ml.
x = corrected volume of gas; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.24	1.6834
6	0.35	0.32	47.92	1.6805
10	0.40	0.37	47.87	1.6801
15	0.47	0.43	47.81	1.6795
20	0.50	0.46	47.78	1.6792
25	0.66	0.60	47.64	1.6780
30	0.80	0.73	47.51	1.6768
35	0.94	0.86	47.38	1.6756
40	1.10	1.01	47.23	1.6742
45	1.31	1.20	47.04	1.6725
50	1.50	1.37	46.87	1.6709
55	1.68	1.54	46.70	1.6693
60	1.90	1.74	46.50	1.6675
65	2.06	1.89	46.35	1.6661
70	2.28	2.09	46.15	1.6642
75	2.40	2.20	46.04	1.6632
81	2.60	2.38	45.86	1.6615
85	2.74	2.51	45.73	1.6603

TABLE XII

Run 8.

Hydrolysis of Triphenylsilane in Piperidine containing 2.75 moles of Water per Liter at 10°.

Weight of sample = 0.5000 gm.; buret temperature = 10°; pressure = 738.3 mm.
Calculated volume of gas at this temperature and pressure = 48.38 ml.
x = corrected volume of gas evolved; a-x = hydrogen remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.38	1.6846
5	0.05	0.05	48.33	1.6842
10	0.15	0.13	48.25	1.6834
15	0.35	0.32	48.06	1.6817
20	0.65	0.59	47.79	1.6793
25	1.00	0.92	47.46	1.6763
30	1.36	1.24	47.14	1.6734
35	1.71	1.57	46.81	1.6703
40	2.05	1.88	46.50	1.6675
45	2.42	2.22	46.16	1.6643
50	2.73	2.50	45.88	1.6617
55	3.04	2.79	45.59	1.6589
60	3.33	3.05	45.33	1.6564
65	3.62	3.32	45.06	1.6538
70	3.91	3.58	44.80	1.6513
75	4.20	3.85	44.53	1.6487
80	4.43	4.05	44.33	1.6467
85	4.71	4.31	44.07	1.6442
90	4.95	4.54	43.84	1.6419
95	5.19	4.75	43.63	1.6398
100	5.46	5.00	43.38	1.6373
105	5.71	5.23	43.15	1.6350
110	6.00	5.50	42.88	1.6322
115	6.23	5.71	42.67	1.6301
120	6.47	5.92	42.46	1.6280
125	6.74	6.17	42.21	1.6254

<u>Results of Kinetic Runs.</u> The rate constants obtained in the kinetic experiments are shown in Table XIII. They were calculated according to the method of least squares as given by Daniels, Mathews, and Williams (5). The error in the rate constant was determined as the root mean square deviation from the calculated slope.

TABLE XIII

Rate Constants for Runs Followed Kinetically

Run No.	Reactants (Toluene used as Solvent)	Rate Constant x 10^4 sec-1
1	R_3SiH in Solution 1	1.287 ± .045
2	R_3SiH in Solution 1	1.273 ± .077
3	R_3SiH in Solution 1	1.272 ± .080
17	R_3SiD in Solution 1	0.938 ± .002
9	R_3SiH in Solution 2	1.903 ± .041
10	R_3SiH in Solution 2	2.092 ± .064
11	R_3SiH in Solution 2	2.054 ± .080
12	R_3SiH in Solution 2	2.071 ± .049
15	R_3SiD in Solution 2	1.466 ± .040

Solution 1 = 20 ml. of Piperidine (.203 mole) and Water (.0551 mole).

Solution 2 = 20 ml. of Piperidine (.203 mole) and D_2O (.0552 mole).

Runs carried out in Solution 2 were competitive hydrolysis.

Runs 1-3 represent hydrolyses of triphenylsilane in a toluene-piperidine-water solution under identical conditions. Consequently, they give an indication of the reproducibility of the method. Run 17 shows the hydrolysis of triphenylsilane-d under the same conditions as those used in Runs 1-3. Only one run was made in order to conserve the triphenylsilane-d for the more important competitive runs to follow. The average ratio of the rates of silicon-deuterium and silicon-hydrogen bond breaking; k_D/k_H, calculated from these runs is $0.73 \pm .04$.

Runs 9-13 show the rates of hydrolyses of triphenylsilane and run 15 shows that of triphenylsilane-d in a toluene-piperidine-deuterium oxide mixture under the same conditions as those of the previous paragraph. Since deuterium oxide exchanges with piperidine

$$C_5H_{10}NH + D_2O \rightleftharpoons C_5H_{10}ND + HOD,$$

in these runs triphenylsilane is reacting with both hydrogen and deuterium compounds simultaneously. Although the rate of reaction of triphenylsilane with piperidine will differ from that with piperidine-d, the first order plot will not be affected because the concentrations of both piperidine and piperidine-d are far in excess to that of the triphenylsilane. The first order plots of these runs up to 50% completion show little or no curvature as can be seen from Fig. 4, page 47, where the data from runs 15 and 12 are plotted.

Consequently pseudo-first order rate constants were calculated for these runs and reported in Table XIII. The ratio of silicon-deuterium and silicon-hydrogen bond breaking, k_D/k_H calculated from runs 10, 11, 12, and 15 was 0.71 ± .04, in excellent agreement with the ratio of 0.73 ± .04 calculated from runs 1, 2, 3, and 17.

The experimental data for all these runs are collected in Tables V-XII on pages 35-42 and Tables XIV-XXII on pages 48-56.

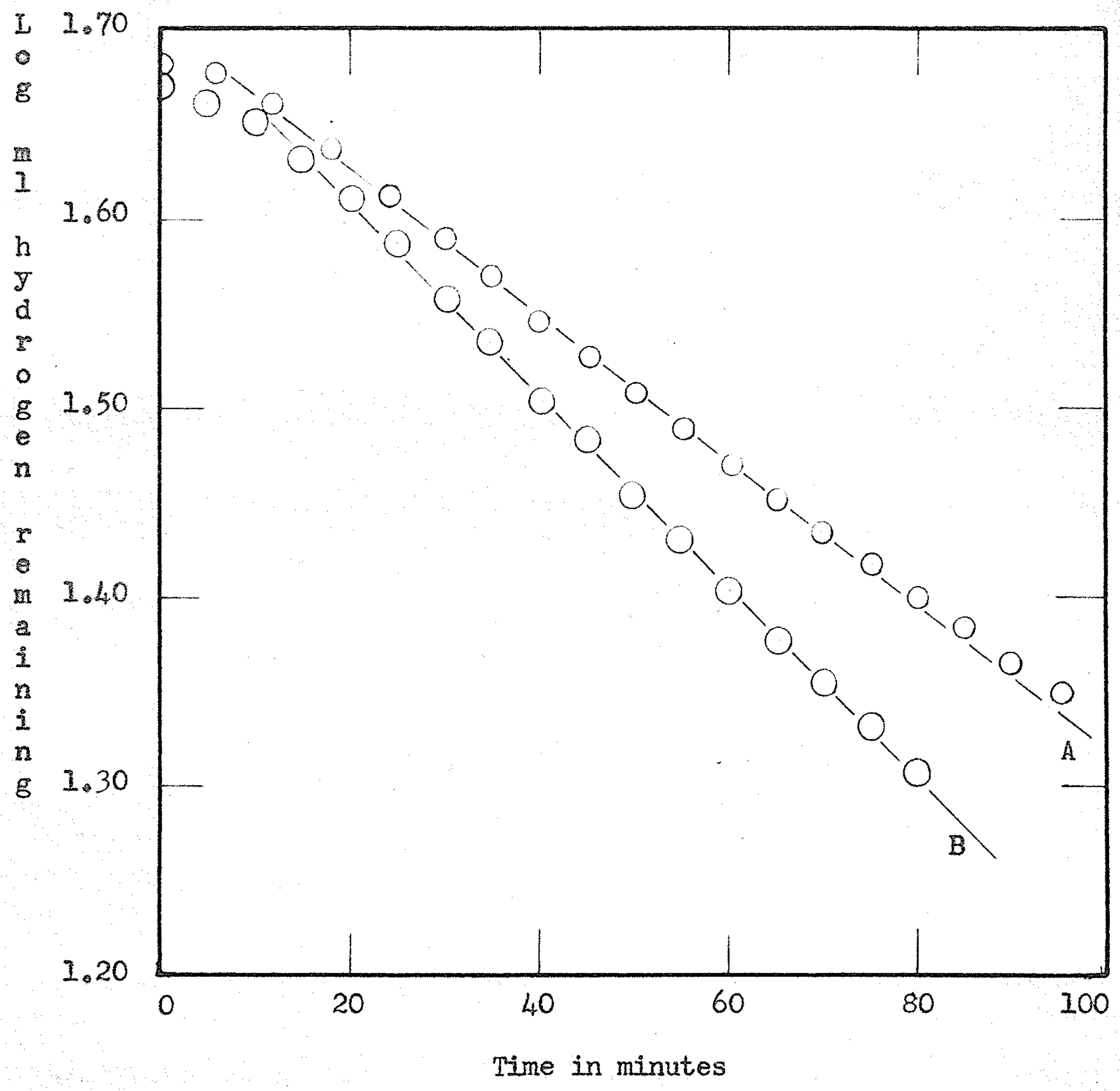


Fig. 3. Relative rates of Hydrolysis of Triphenylsilane-d, A, and Triphenylsilane, B, in Piperidine containing 2.75 mole of H_2O per Liter.

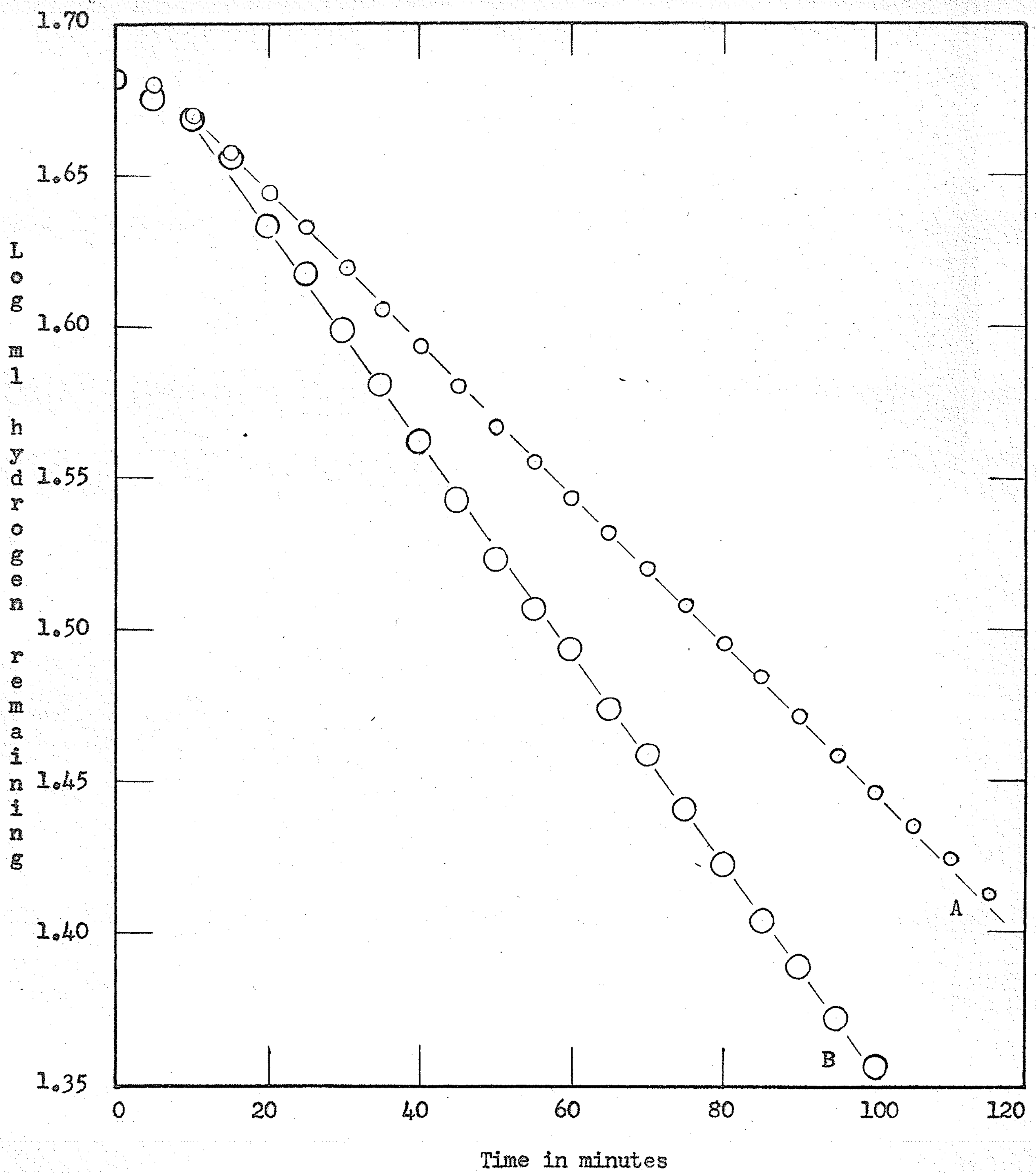


Fig. 4. Relative rates of Hydrolysis of Triphenylsilane-d, A, and Triphenylsilane, B, in Piperidine containing 2.77 mole of D_2O per Liter.

TABLE XIV

Run 9.

Hydrolysis of Triphenylsilane in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 746.4 mm.
Calculated volume of gas at this temperature and pressure = 47.91 ml.
x = corrected volume of HD evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	47.91	1.6804
5	0.70	0.64	47.27	1.6745
10	1.50	1.37	46.54	1.6678
15	3.30	3.02	44.89	1.6522
20	5.30	4.85	43.06	1.6341
25	7.60	6.96	40.95	1.6122
30	10.10	9.25	38.66	1.5873
35	12.70	11.45	36.46	1.5618
40	14.70	13.42	34.49	1.5377
45	16.50	15.11	32.80	1.5159
50	18.60	17.04	30.87	1.4896
55	20.80	19.15	28.76	1.4588
60	22.00	20.15	27.76	1.4434
65	23.90	21.89	26.02	1.4153
70	25.60	23.45	24.46	1.3885
75	27.10	24.82	23.09	1.3634
80	28.00	25.65	22.26	1.3476
85	29.40	26.93	20.98	1.3218
90	30.40	27.85	20.06	1.3023
95	31.30	28.67	19.24	1.2842
100	32.20	29.50	18.41	1.2650
105	33.10	30.32	17.59	1.2452
110	34.00	31.14	16.77	1.2245
115	34.80	31.88	16.03	1.2049
120	35.40	32.43	15.48	1.1897
125	36.10	33.07	14.84	1.1715

TABLE XV

Run 10

Hydrolysis of Triphenylsilane in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of Sample = 0.5000 gm.; buret temperature = 25°; pressure = 733.7 mm.
Calculated volume of gas at this temperature and pressure = 48.73 ml.
x = corrected volume of HD evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.73	1.6878
5	0.80	0.73	48.00	1.6812
10	2.00	1.83	46.90	1.6712
15	4.20	3.85	44.88	1.6512
20	7.00	6.41	42.32	1.6265
25	9.80	8.98	39.75	1.5993
30	12.60	11.54	37.19	1.5704
35	16.00	14.66	34.07	1.5324
40	18.20	16.67	32.06	1.5059
45	20.40	18.69	30.04	1.4776
50	22.50	20.61	28.08	1.4484
55	24.20	22.17	26.56	1.4242
60	25.50	23.36	25.37	1.4043
65	27.00	24.73	24.00	1.3802
70	28.40	26.01	22.72	1.3564
75	29.80	27.30	21.45	1.3310
80	31.00	28.40	20.33	1.3081
85	32.00	29.31	19.42	1.2882
90	32.80	30.04	18.69	1.2716
95	33.60	30.78	17.95	1.2541
100	34.40	31.51	17.22	1.2340
105	35.30	32.33	16.40	1.2148
110	36.30	33.25	15.48	1.1897
115	37.20	34.08	14.65	1.1659
120	38.00	34.81	13.92	1.1436

TABLE XVI

Run 11.

Hydrolysis of Triphenylsilane in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 738.5 mm.
Calculated volume of gas at this temperature and pressure = 48.42 ml.
x = corrected volume of HD evolved; a-x = volume of HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.42	1.6850
5	0.90	0.82	47.60	1.6776
10	4.20	3.85	44.57	1.6491
15	7.20	6.60	41.82	1.6214
20	10.60	9.71	38.71	1.5878
25	12.90	11.82	36.60	1.5635
30	15.30	14.01	34.41	1.5367
35	17.50	16.03	32.39	1.5104
40	19.50	17.86	30.56	1.4852
45	21.30	19.52	28.90	1.4609
50	23.10	21.16	27.26	1.4355
55	24.80	22.72	25.70	1.4099
60	26.20	24.00	24.42	1.3878
65	27.60	25.28	23.16	1.3647
70	28.80	26.38	22.04	1.3432
75	30.00	27.48	20.94	1.3209
80	31.10	28.49	19.93	1.2996
85	32.10	29.40	19.02	1.2792
90	33.00	30.23	18.19	1.2596
95	34.00	31.14	17.28	1.2375
100	34.90	31.97	16.45	1.2161

TABLE XVII

Run 12.

Hydrolysis of Triphenylsilane in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of sample = 0.5000 gms.; buret temperature = 25°; pressure = 739.8 mm.
Calculated volume of gas at this temperature and pressure = 48.31 mls.
x = corrected volume of HD evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.31	1.6840
5	0.70	0.64	47.67	1.6782
10	1.30	1.19	47.12	1.6732
15	2.40	2.20	46.11	1.6638
20	3.80	3.48	44.83	1.6516
25	5.70	5.22	43.09	1.6344
30	7.40	6.78	41.53	1.6183
35	10.60	9.71	38.60	1.5866
40	13.40	12.27	36.04	1.5568
45	15.40	14.11	34.20	1.5340
50	18.10	16.58	31.73	1.5015
55	19.40	17.77	30.54	1.4849
60	21.70	19.88	28.43	1.4538
65	23.30	21.34	26.97	1.4309
70	25.10	23.00	25.31	1.4033
75	26.70	24.46	23.85	1.3775
80	27.80	25.46	22.85	1.3589
85	29.20	26.75	21.56	1.3336
90	30.50	27.94	20.37	1.3090

TABLE XVIII

Run 13.

Competitive Hydrolysis of Triphenylsilane and Triphenylsilane-d in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gm. each of Triphenylsilane and Triphenylsilane-d. Buret temperature = 25°; pressure = 746 mm. Calculated volume of gas at this temperature and pressure = 95.84 ml.;
x = corrected volume of gas evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	95.84	1.9816
5	1.40	1.28	94.56	1.9757
10	7.80	7.15	88.69	1.9478
15	15.20	13.92	81.92	1.9134
20	22.20	20.34	75.50	1.8779
25	29.20	26.75	69.09	1.8394
30	34.00	31.14	64.70	1.8109
35	38.40	35.18	60.66	1.7829
40	42.40	38.84	57.00	1.7559
45	46.00	42.14	53.70	1.7300
48	47.60	43.60	52.24	1.7180

TABLE XIX

Run 14.

Competitive Hydrolysis of Triphenylsilane and Triphenylsilane-d in Piperidine containing 2.75 moles Water per Liter at 25°.

Weight of sample = 0.5000 gm. each of Triphenylsilane and Triphenylsilane-d.
Buret temperature = 25°; pressure = 740.4 mm.
Calculated volume of gas at this pressure and temperature = 96.50 ml.
x = corrected volume of gas evolved; a-x = ml of HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	96.50	1.9845
5	0.80	0.73	95.77	1.9811
10	2.70	2.47	94.03	1.9732
15	6.10	5.59	90.91	1.9586
20	10.50	9.62	86.88	1.9389
25	15.40	14.11	82.39	1.9159
30	20.80	19.15	77.35	1.8885
35	31.80	29.13	67.37	1.8285
40	38.00	34.81	61.69	1.7902
45	41.50	38.02	58.48	1.7670
47	42.50	38.93	57.57	1.7602

TABLE XX

Run 15.

Hydrolysis of Triphenylsilane-*d* in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 737.9 mm.
Calculated volume of gas at this temperature and pressure = 48.38 mls.
x = corrected volume of HD evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.38	1.6846
3	0.50	0.46	47.92	1.6805
6	0.80	0.73	47.65	1.6781
9	1.50	1.37	47.01	1.6722
12	2.60	2.48	45.90	1.6618
15	4.00	3.66	44.72	1.6505
18	5.30	4.85	43.53	1.6388
21	6.60	6.05	42.33	1.6266
24	8.00	7.33	41.05	1.6133
27	9.20	8.43	39.95	1.6015
30	10.30	9.44	38.94	1.5904
35	12.20	11.18	37.20	1.5705
40	14.20	13.01	35.37	1.5487
45	16.00	14.66	33.72	1.5279
50	17.60	16.12	32.26	1.5087
55	19.10	17.50	30.88	1.4897
60	20.50	18.78	29.60	1.4713
65	21.70	19.88	28.50	1.4548
70	23.00	21.07	27.31	1.4364
75	24.20	22.17	26.21	1.4185
80	25.30	23.17	25.21	1.4016
85	26.30	24.09	24.29	1.3854
90	27.30	25.01	23.37	1.3687
95	28.20	25.84	22.54	1.3530
100	29.20	26.75	21.63	1.3351
105	30.10	27.57	20.81	1.3183
110	31.00	28.40	19.98	1.3007
115	31.90	29.22	19.16	1.2823
120	32.70	29.95	18.43	1.2655
125	33.40	30.60	17.78	1.2500
130	34.10	31.24	17.14	1.2340

TABLE XXI

Run 16.

Hydrolysis of Triphenylsilane-d in Piperidine containing 2.77 moles of Deuterium Oxide per Liter at 25°.

Weight of sample = 0.2000 gm.; buret temperature = 25°; pressure = 741.2 mm.
Calculated volume of gas at this temperature and pressure = 19.29 ml.
x = corrected volume of gas evolved; a-x = HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	19.29	1.2853
5	0.20	0.18	19.11	1.2812
10	0.30	0.27	19.02	1.2792
15	0.50	0.46	18.83	1.2749
20	1.00	0.92	18.37	1.2641
25	1.60	1.47	17.82	1.2509
30	2.30	2.11	17.18	1.2350
35	2.70	2.47	16.82	1.2258
40	3.40	3.11	16.18	1.2089
45	3.80	3.48	15.81	1.1990
50	4.40	4.03	15.26	1.1835
55	4.90	4.49	14.80	1.1703
60	5.50	5.04	14.25	1.1538
65	6.00	5.50	13.79	1.1396
70	6.50	5.95	13.34	1.1252
75	6.90	6.32	12.97	1.1130
80	7.40	6.78	12.51	1.0972
85	7.90	7.24	12.05	1.0809
92	8.50	7.79	11.50	1.0607

TABLE XXII

Run 17.

Hydrolysis of Triphenylsilane-d in Piperidine containing 2.75 moles of Water per Liter at 25°.

Weight of sample = 0.5000 gm.; buret temperature = 25°; pressure = 742.5 mm.
Calculated volume of gas at this temperature and pressure = 48.15 ml.
x = corrected volume of HD; a-x = volume of HD remaining.

Time Min.	Buret Reading (ml.)	x (ml.)	a-x (ml.)	log a-x
0	0.00	0.00	48.15	1.6825
5	0.70	0.64	47.51	1.6768
10	1.40	1.28	46.87	1.6709
15	2.80	2.56	45.59	1.6589
20	4.20	3.85	44.30	1.6464
25	5.60	5.13	43.02	1.6337
30	7.00	6.41	41.74	1.6205
35	8.40	7.70	40.45	1.6069
40	9.70	8.89	39.26	1.5940
45	11.00	10.08	38.07	1.5806
50	12.20	11.18	36.97	1.5678
55	13.30	12.18	35.97	1.5560
60	14.40	13.19	34.96	1.5436
65	15.40	14.11	34.04	1.5320
70	16.40	15.02	33.13	1.5204
75	17.30	15.85	32.30	1.5092
80	18.30	16.76	31.39	1.4967
85	19.20	17.59	30.56	1.4852
90	20.20	18.50	29.65	1.4720
95	21.10	19.33	28.82	1.4597
100	22.00	20.15	28.00	1.4472
105	22.80	20.88	27.27	1.4357
110	23.50	21.53	26.62	1.4252
115	24.20	22.17	25.98	1.4147
120	24.90	22.81	25.34	1.4038
125	25.60	23.45	24.70	1.3927

Competitive Runs.

A more reliable method of measuring the ratio of the rates of silicon-deuterium and silicon-hydrogen bond breaking than the kinetic one discussed in the previous section is to let triphenylsilane-d and triphenylsilane compete for protons in the same reaction mixture according to the equations

$$OH^- + R_3SiD + PH \longrightarrow R_3SiOH + HD + P^-$$

and $$OH^- + R_3SiH + PH \longrightarrow R_3SiOH + H_2 + P^-$$

where PH represents piperidine and R represents the phenyl group. The ratio of the rates of deuteron and proton abstraction from the solvent can be obtained in a similar way from the competitions:

$$OH^- + R_3SiH + PD \longrightarrow R_3SiOH + HD + P^-$$

and $$OH^- + R_3SiH + PH \longrightarrow R_3SiOH + H_2 + P^-$$

If these reactions are stopped before completion, then the ratio of the rates of formation of HD and H_2 in each case can be calculated from the ratio of deuterium and hydrogen in the gas obtained from the reaction. This section records the measurement of each of these ratios by means of the appropriate competition.

In this investigation the ratio of deuterium and hydrogen in the gas produced by the competition was determined by oxidizing the gas to water and measuring the density of the water. In carrying out these experiments there were five steps; (1) hydrolysis, in which the reactants were mixed and a suitable amount of gas collected; (2) drying the gas, in which the solvent vapors were removed from the gas; (3) oxidation of hydrogen, in which the gas was oxidized to water by hot copper oxide; (4) purification of water samples, in which the water was refluxed with alkaline permanganate and repeatedly distilled; and (5) determination of the density of the water samples, which was carried out by allowing a drop of the purified water to find its level in a column containing a mixture of organic solvents having a linear vertical gradient of densities. Each of these stages will be discussed in detail below.

Hydrolysis. The apparatus employed for the competitive hydrolyses was the same as that used in the kinetic runs. The temperature was maintained at 25.000 ± .006°C. and the Vari-ac controlling the amount of agitation of the reaction buret was set at 35 volts. In these runs however a second buret was attached to the reaction buret at D, Figure 1, prior to the commencement of a run. Thus when the desired amount of gas had been collected, it could be separated from the reaction mixture rapidly and completely by raising the mercury in the reaction buret until all the gas was excluded.

For competition between triphenylsilane-d and triphenylsilane, 0.5000 gm. (0.00192 mole) of each of these substances were dissolved together in 20 ml. (.1874 mole) of toluene in the separatory funnel A, Figure 1. To this was added 40 ml. of a solution containing 0.406 moles of piperidine and 0.1102 moles of water. These were mixed thoroughly and drawn into the reaction buret by lowering the mercury.

The mercury was then raised so that the solution rose to the stopcock thus excluding all air, and the stopcock was closed. When the reaction was about 50% complete the stopcock was turned to connect the reaction buret to the second buret (which contained only mercury) through D, Figure 1, and the mercury levels were manipulated so as to transfer all the gas into the second buret.

For competition between piperidine-d and piperidine a mixture of these substances was required. This was obtained by dissolving 5 ml. (.276 mole) of deuterium oxide (99.73 atom percent deuterium) in 100 ml. (1.015 mole) of piperidine and allowing the mixture to stand until the reactions

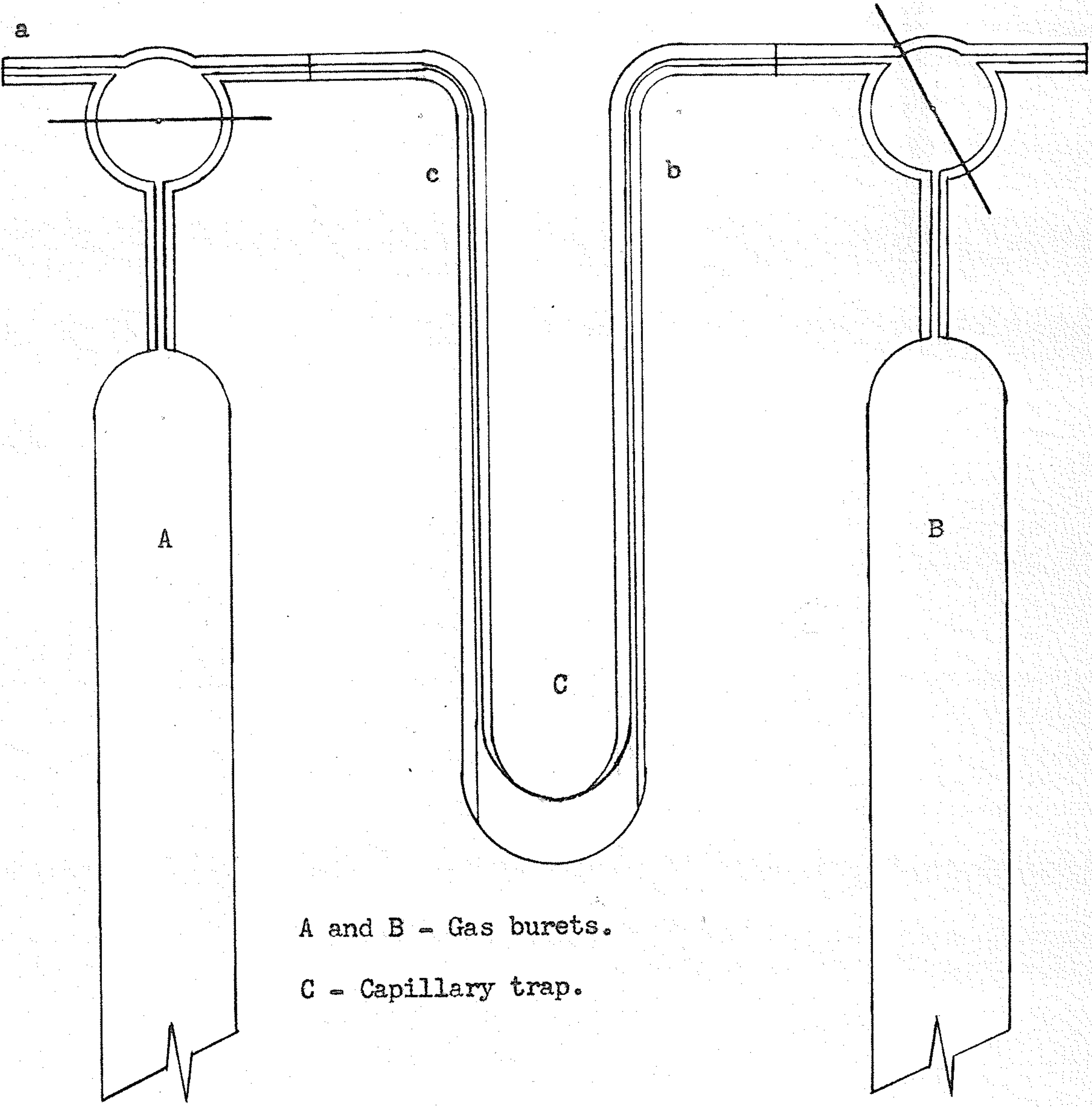
$$C_5H_{10}NH + D_2O \rightleftharpoons C_5H_{10}ND + HOD$$

$$2HOD \rightleftharpoons H_2O + D_2O$$

had reached equilibrium, which is an almost instantaneous process. The relative concentrations of piperidine and piperidine-d in this mixture were calculated by a method to be described later. The hydrolysis was carried out exactly as in the previous case except that 0.5000 gm. (0.00192 mole) of triphenylsilane was treated with 10 ml. of toluene, and 20 ml. of the piperidine-deuterium oxide solution described above.

Drying the Gas Samples. In carrying out the hydrolysis, the silane was dissolved in toluene and hydrolyzed by a piperidine-water solution. The volume occupied by the product gases included the vapors of toluene and piperidine which at room temperature would contribute a significant portion of the final volume. The calculation of the relative rate of hydrolysis involved the percent completion of the competitive runs. The calculation of the rate constants also depended on the volume of hydrogen gas evolved. Therefore the removal of the solvent vapors was necessary to eliminate the error in the volumes of gas collected. The removal was accomplished by passing the hydrogen gas through a Dry Ice-acetone trap.

The volume of gas to be dried was recorded by employing a cathetometer to check the mercury levels in the buret and the reservoir. The two burets and the trap were arranged as shown in Fig. 5. The trap was constructed of Pyrex glass capillary tubing in the form of a U-tube having an enlarged bulb. The stopcock of buret (A) containing the gas sample was turned so that buret (B) was open to the atmosphere through the trap. The mercury level in Buret (B) was raised so that the mercury filled the trap and the connecting tube of buret (A) to a point (a) beyond the stopcock. This excluded all the air in the system. The stopcock on buret (A) was turned to connect both burets and the gas was forced out until the mercury level was beyond the bulb of the trap at point (b). This was necessary since the temperature obtained from the Dry Ice-acetone mixture was sufficiently low to solidify the mercury in the trap.



A and B - Gas burets.

C - Capillary trap.

Fig. 5. Hydrogen gas drying Apparatus.

The trap was immersed in the freezing mixture and by manipulation of the mercury levels the gas was flushed back and forth through the trap several times. The level of the mercury was not allowed to extend into the trap during the flushing process. To complete the transfer the mercury level of buret (A) was raised to point (c). The freezing mixture was then removed and the mercury level raised further until the mercury extended through the trap to the stopcock of the buret (B). The stopcock was closed and the apparatus disconnected. The dried volume was recorded and the gas was set aside for the oxidation process.

Oxidation of Hydrogen. The oxidation apparatus consisted of a three unit macro furnace having all three units set at 370°C. The combustion tube was of Vycor glass and was filled with copper oxide. This tube had a standard taper glass joint as an outlet and an additional capillary tube opening at the inlet end. In carrying out the hydrolysis of the silane in a 100 ml. gas buret, the maximum volume of hydrogen obtainable was 70 ml. since the volume occupied by the reaction solution was 30 ml. The water sample obtained from this volume would be extremely small, making manipulation difficult and the results susceptible to large error. Therefore the samples were diluted with hydrogen gas to a volume of 600 ml. The hydrogen used for this dilution had a purity of 99.9% so that no further purification was carried out on it. This volume of gas gave a water sample of approximately 0.4 gm. The dilution buret, having a capacity of 700 ml., was attached to the combustion tube inlet by one end of a three-way stopcock. The other end of the stopcock was used for attachment of the transfer buret containing the dried gas sample.

The additional capillary inlet carried a stream of nitrogen gas for the purpose of flushing the water vapor into the collection tube. The nitrogen gas was first conveyed from the cylinder through a bubbler system to remove any water present in the nitrogen. The bubbler system consisted of two concentrated sulphuric acid bubblers, a calcium chloride and an Anhydrone drying tube arranged in that order. The bubblers also acted as a method of measuring the rate of flow of nitrogen into the combustion tube.

The water produced in this oxidation was collected in a Pyrex glass U-tube immersed in a Dry Ice-acetone mixture. The U-tube had a standard taper joint for attachment to the combustion tube. The other end was drawn to a capillary through which the nitrogen gas escaped. The capillary at this end was a preventative measure against the infusion of water vapor from the atmosphere.

Procedure for an oxidation was as follows. The furnace was plugged in and allowed to heat for about half an hour before the oxidation was started. The nitrogen gas was passed through the system at approximately one bubble per second to clear the apparatus of any water that had infused into the system. The collection tube was weighed and attached to the combustion tube. The transfer buret, containing the dried gas, was attached to the dilution buret and the gas was transfered by manipulation of the mercury levels in the burets.

The dilution buret was graduated to 5 ml. divisions so that the actual volume measurements were carried out in the transfer buret which was graduated to 0.2 ml. divisions. This was accomplished by attaching the hydrogen gas line to this buret, filling to 100 ml. and then transfering to the dilution buret. This process was repeated until approximately 600 ml. of gas were in the dilution buret.

The collection tube was now immersed in the freezing mixture and the stopcock on the dilution buret turned to connect it with the combustion tube. The hydrogen gas was then slowly passed into the combustion tube by raising the mercury level in the buret. The rate of passage of gas into the combustion tube was such that the process required two hours to complete. When all the hydrogen had passed into the combustion tube the stopcock was turned, cutting out the buret. The nitrogen was allowed to flow an additional twenty minutes to insure that all the water vapor had been carried into the collection tube. The capillary opening of this tube was sealed and the tube was removed, stoppered, and weighed.

The reproducibility of this phase of the work was determined by oxidizing the gas samples obtained from the kinetic determinations and checking the experimental weight against the theoretical weight of water. Five such determinations were carried out and the results are tabulated below.

TABLE XXIII

Comparison of Theoretical and Actual Weight of Water Samples.

No.	Volume ml. of H_2.	Temp. °C.	Pressure (mm.)	Exp. Wt. of Water (gm.)	Theoretical Wt. of Water (gm.)	Percent Deviation
1	600	24.5	749.7	.4382	.4375	+ 0.16
2	600	25	732.2	.4226	.4236	- 0.23
3	600	24	740.2	.4290	.4304	- 0.32
4	606	28	735.9	.4258	.4266	- 0.19
5	604	24	745.6	.4379	.4378	+ 0.023

Purification of Water Samples. The water samples obtained from the oxidation process were purified by the method described by A. S. Keston, D. Rittenberg, and R. Schoenheimer (15). The purification apparatus consisted of a train of Pyrex glass U-tubes, having standard taper joints. The U-tubes were cleaned with a sulphuric acid-potassium dichromate cleaning solution, washed with ammonium hydroxide and rinsed several times with distilled water. They were dried in an oven at 110°C. After the apparatus had been assembled it was thoroughly flamed.

The U-tubes were arranged as shown in Fig. 6. The last tube was fitted with a drying tube, filled with Anhydrone, to prevent infusion of water vapor. The U-tube, No. 2 in Fig. 6, was placed in a Dry Ice-acetone mixture, and small amounts of calcium oxide and potassium permanganate were introduced into this tube to act as purifying agents. Calcium oxide was used in place of sodium hydroxide to prevent deuterium from the water sample exchanging with the hydroxyl group.

The U-tube, No. 1 in Fig. 6, containing the water sample was attached to the train. Using a low flame, the water was distilled into the No. 2 U-tube. After the distillation had been completed, the first tube was removed and the system stoppered. The Dry Ice-acetone mixture was then moved to the No. 3 U-tube and the water distilled into it. This procedure was continued until the water sample had been carried through seven distillations. The sample was then transfered into a serum vial and sealed with a self-sealing

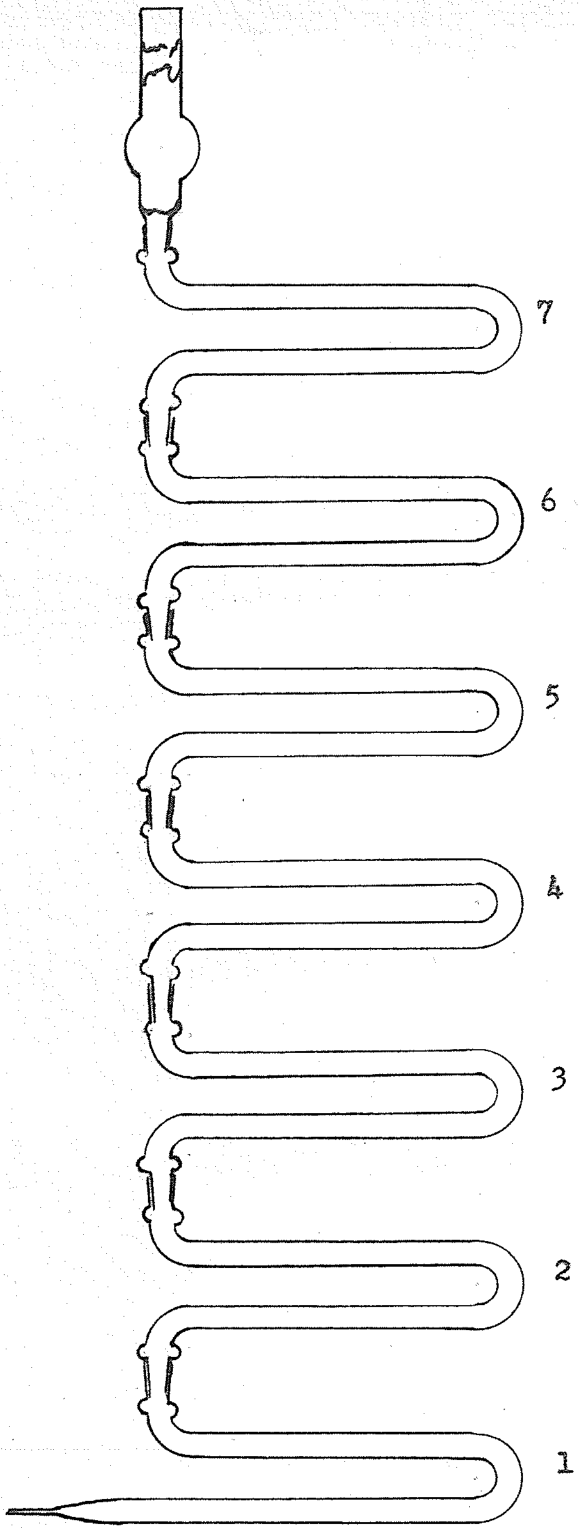


Fig. 6. Apparatus for Purification of Water Samples.

rubber stopper. The loss in the samples due to the distillations was small; however, the exact magnitude of this loss was not determined.

Determination of the Density of the Water Samples. The gradient density tube method of C. Anfinsen (1) was employed to determine the deuterium content of the water samples obtained from the competitive runs. This method was selected for its simplicity and accuracy. It is based on Fick's principle that a linear gradient of densities is produced at the juncture of two miscible liquids of unequal specific gravities. The liquids employed were two kerosene-bromobenzene solutions having densities of 0.99 and 1.02. The solution having a density of 0.99 is slightly lighter than water whereas the solution of density 1.02 is heavier than a water solution containing 10% deuterium oxide. This gave the density tube a working range of 10% deuterium oxide in the water samples. A gradient tube prepared by this method could maintain a linear gradient of densities for a period of six to twelve months providing reasonable care was exercised in its use.

The gradient tube as shown in Fig. 7 was mounted in a glass-fronted thermostat maintained at 25.000 ± .006°C. The tube was filled to the midpoint (A in the diagram) of the column with the kerosene-bromobenzene solution of density 1.02. The lighter solution was then layered over this by gentle introduction through a funnel kept at a level slightly below the surface of the solution until the tube was filled. To produce the linear gradient, the two solutions

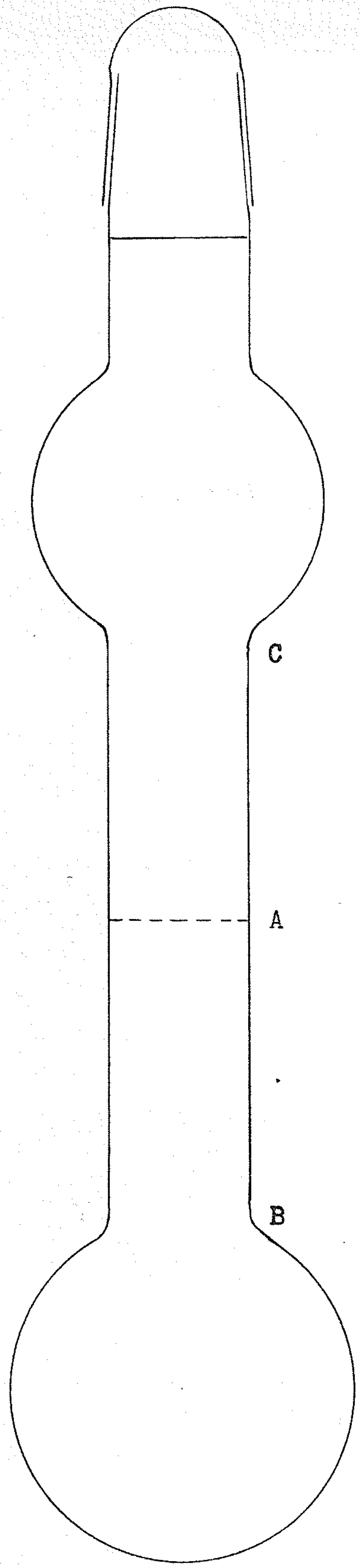
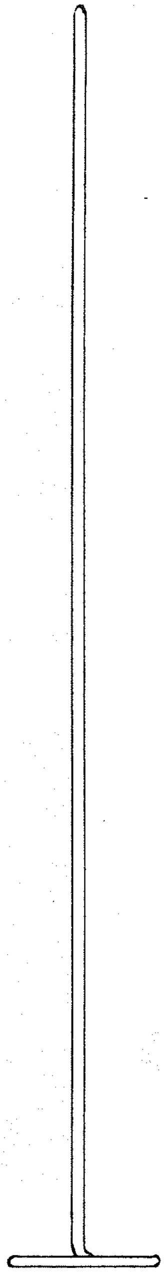


Fig. 7. Gradient Density Tube.



Glass Stirrer.

were stirred with a glass spiral stirrer starting at the line of juncture (A in diagram) and stirring with strokes of increasing length so that on the tenth stroke the entire length of the column was traversed (B to C in the diagram). The tube was then allowed two days in which to attain equilibrium.

The drop being introduced into the density tube was withdrawn from the sealed serum vial with a hypodermic needle. The needle was inserted into the sample through the self-sealing stopper. This procedure eliminated the possibility of contaminating the sample on its coming in contact with the atmosphere. A capillary tube extension was attached to the needle to withdraw a sufficient volume of the sample. The capillary extension had a $\frac{1}{4}$ mm. bore and was 10 cm. in length. One end of this tube was ground to fit the needle opening. The needles and extensions were washed several times with distilled water, dried in an oven, and cooled in a desiccator. During use they were not cleaned but rinsed with the solution to be introduced into the tube.

A rubber policeman was used on the capillary extension to draw the solution into the needle. The needle was inserted into the sample through the rubber stopper and the solution drawn halfway up the capillary extension by releasing the pressure on the policeman. The needle was withdrawn from the vial and emptied. It was then refilled and introduced into the density tube with the tip just below the surface of the liquid. By applying gentle pressure to the policeman the drop formed and fell away from the needle. The drops formed by this procedure were consistent in size, being 3 mm. in diameter.

The standard drops were introduced on the right hand side of the tube and the unknown drops on the left hand side. The order of introduction of the standards was the heaviest first to prevent collision on their downward motion to the equilibrium levels. The drops were allowed two hours to attain their levels which were recorded by a cathetometer accurate to 0.1 mm. The reading of the top and bottom of each drop was taken three times at intervals of ten minutes. The mean value of the center of each drop was used in the calculation on the percent deuterium oxide. The standards were chosen in such a manner that one was above and one below the level of the unknown drop. The percent deuterium oxide and the vertical difference in the levels of the two standard drops as well as the level of the sample were known. The calculation of the percent deuterium oxide in the sample was then a simple interpolation.

The water drops were removed from the density tube by introduction of the glass rod which had a piece of moist filter paper wrapped around the tip. The water drop on coming in contact with the filter paper was absorbed. After removal of all the drops the tube was allowed twelve hours in which to regain its linear gradient of densities.

The linearity of the gradient was checked by introduction of all the standard solutions, allowing them to attain their equilibrium positions and recording these with the cathetometer. A plot shown in Fig. 8, was made from the cathetometer readings versus the percent deuterium oxide to show this linear relationship. The gradient did not remain constant; the levels were found to alter with fluctuations of pressure as well as with turbulences within the tube solution due to the vibrations of the stirrer. This resulted in the standards being introduced with all samples.

A loss of deuterium due to exchange with the hydrogen in the apparatus occurred during the course of the oxidation and purification processes. The magnitude of this loss was determined by vaporizing the No. 5 and No. 4 standard solutions in the combustion tube and collecting the water in the collection tube. The water was then subjected to the purification process and its density determined. The loss observed was 1.5% of the deuterium oxide present in each of the standard solutions. This result was employed as a correction in all the samples from competitive runs.

To determine if the variation in the densities of the tube affected the final percent deuterium oxide in the samples, a second density determination was carried out on some of the samples. The deviations observed between the two values were small as can be seen from the table of results for this part of the work, Table XXIV.

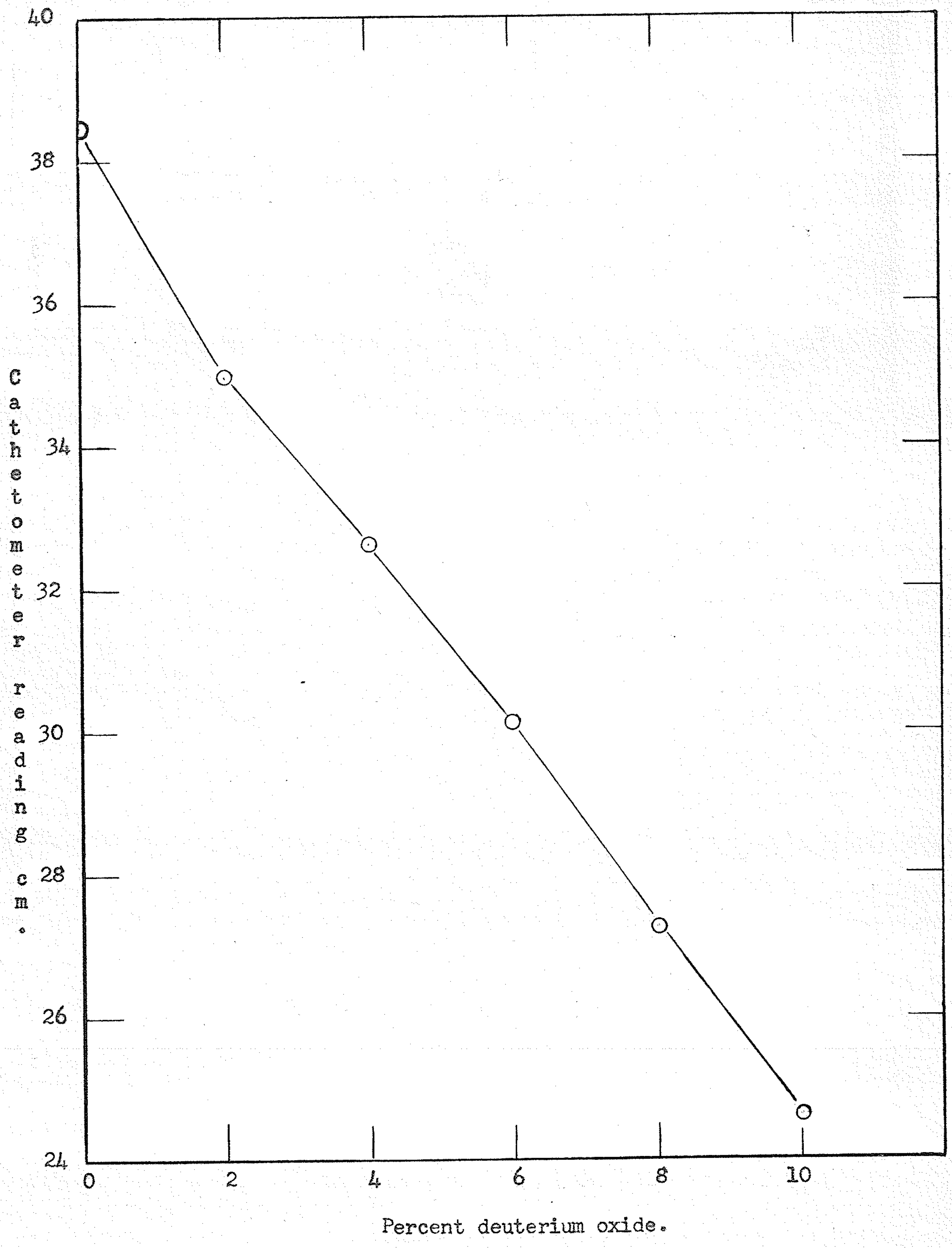


Fig. 8. Plot of Cathetometer Reading Versus Percent Deuterium Oxide.

TABLE XXIV

Percent Deuterium Oxide in the Analyzed Samples.

Sample from Run No.	Experimental % D_2O Trial #1	Experimental % D_2O Trial #2	Mean Corrected[a] % D_2O.
No. 5 Standard Solution	7.849	7.854	---
No. 4 Standard Solution	5.893	5.894	---
Deuterium Analysis of Silane-d.	1.507	1.505	1.530
8	1.101	---	1.118
9	0.563	---	0.571
10	0.775	0.775	0.783
11	1.519	---	1.542
12	1.388	1.390	1.410
15	4.911	4.925	4.992
16	1.216	1.218	1.235
17	3.789	---	3.847

[a] Mean Corrected % D_2O was the mean value of Trials #1 and #2, including the correction for dilution of deuterium in the oxidation and purification processes.

<u>Results of Competitive Runs.</u> The competitive runs carried out during this investigation were:-

(1). Competition between triphenylsilane-<u>d</u> and triphenylsilane,

- (a) triphenylsilane-<u>d</u> and triphenylsilane in piperidine-water solution;

(2). Competition between piperidine-<u>d</u> and piperidine,

- (a) triphenylsilane in piperidine-deuterium oxide solution;
- (b) triphenylsilane-<u>d</u> in the piperidine-deuterium oxide solution.

The ratio of k_D/k_H for all competitive runs was calculated from the following equation

$$\frac{k_D}{k_H} = \frac{\log(1 + 1/X) - \log\left[(1 + 1/X) - P(1 + 1/A)\right]}{\log(1 + X) - \log\left[(1 + X) - P(1 + A)\right]}$$

where A = the ratio of deuterium to hydrogen in the starting material;

X = the ratio of deuterium to hydrogen in the products;

P = the portion of reaction completed (ratio of products to reactants).

This equation was derived from the rate constants of the two species that are in competition. Thus

$$k_D t = \ln \frac{a'}{a'-x'} \qquad \text{and } k_H t = \ln \frac{a}{a-x}$$

represent the rate expressions for the deutero and normal silane. a' and a are the initial concentrations and a'-x' and a-x are the concentrations at time t. The ratio

$$\frac{k_D}{k_H} = \frac{\log \frac{a'}{a'-x'}}{\log \frac{a}{a-x}}$$

can be shown to be equivalent to the above form if the following substitutions are carried out.

$$\frac{a'}{a} = A \qquad \frac{x'}{x} = X \qquad \text{and } P = \frac{x + x'}{a + a'}$$

The probable error in the ratio was obtained employing the method described by Daniels, Mathews, and Williams (5). The root mean square deviation was obtained from the sum of the partial derivatives of the above equation with respect to the variables X, A, and P. The error in the ratio was found to be ± 0.02 employing the experimental errors of 1%, .04%, and 4% assigned to X, A, and P respectively. The derivation of the probable error equation and the calculation are omitted due to their lengthy and cumbersome mathematical treatment.

The competitive runs of type (la) proceeded according to the following equations

$$OH^- + R_3SiH + PH \longrightarrow R_3SiOH + H_2 + P^-$$

and $$OH^- + R_3SiD + PH \longrightarrow R_3SiOH + HD + P^-$$

The evolved gas would be a mixture of H_2 and HD which when oxidized produces H_2O, HOD and D_2O. Density determination on this water gave the total atom percent deuterium present in all forms. An allowance had to be made for the presence of triphenylsilane in the triphenylsilane-d.

The calculation of the ratio for the competitive runs of types (2a) and (2b) required preliminary calculations. In these runs the water was replaced by deuterium oxide in the hydrolyzing solution. The concentrations of the reactants after the establishment of the equilibrium were obtained from the following conditions

$$(1)\quad \mathrm{PH} + \mathrm{D_2O} \overset{K}{\rightleftharpoons} \mathrm{PD} + \mathrm{HOD}$$

where PH represents piperidine and PD is the deuterated piperidine. The equilibrium constant for equation (1) can be written as

$$K = \frac{[\mathrm{PD}][\mathrm{HOD}]}{[\mathrm{PH}][\mathrm{D_2O}]}$$

The deuterium hydrogen oxide produced by this equilibrium is involved in a further equilibrium

$$(2)\quad \mathrm{H_2O} + \mathrm{D_2O} \overset{K'}{\rightleftharpoons} 2\mathrm{HOD}$$

or

$$K' = \frac{[\mathrm{HOD}]^2}{[\mathrm{H_2O}][\mathrm{D_2O}]}$$

The equilibrium constant for the reaction (2) is known to be 3.80 (17, 25) but that for the piperidine-deuterium oxide is not known.

An approximation was therefore made using the constant of a similar equilibrium involving the nitrogen atom

$$ND_2H + D_2O \rightleftharpoons ND_3 + HOD \qquad (a)$$

for which the equilibrium constant was known to be 0.72 (17). The equilibrium constant for the reaction

$$D_2HO^+ + D_2O \rightleftharpoons D_3O^+ + HOD \qquad (b)$$

was known to be 0.76 (25). Since the difference in the equilibrium constants for the two exchange reactions (a) and (b) is only 5% even though the exchange is occurring on the oxygen atom in one case and on the nitrogen in the other, it seems reasonable to suppose that the difference in equilibrium constants for reactions (1) and (a) above, in which the exchange is occurring on nitrogen in both cases, would be at least no greater than 5%[4]. Therefore the value of 0.72 was used as the equilibrium constant for the reaction (1).

Further, the known initial quantities of the reactants provided the following conditions

(3) $PH + PD = .203$ mole

where .203 is the moles of piperidine used.

(4) $HOD + H_2O + D_2O = .0552$ mole

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[4] It may be noted that an error of 5% in K has a smaller effect on k_D/k_H than the experimental error (1%) assigned to the value of X (page 76).

where .0552 is the initial moles of D_2O used.

(5) $2D_2O + HOD + PD = .1104$ mole.

where .1104 is the gm. atoms of deuterium in the deuterium oxide. These five relations were incorporated into the cubic equation,

$$PD^3 + .2771\ PD^2 + .008795\ PD - .001489 = 0$$

which yielded the following concentrations for the reactants after the establishment of the equilibrium.

deuterated piperidine (PD) = .0551 mole.
deuterium oxide (D_2O) = .0139 mole.
piperidine (PH) = .1479 mole.
water (H_2O) = .0140 mole.
deuterium hydrogen oxide (HOD) = .0273 mole.

Thus A, X, and P could be calculated and a value of k_D/k_H obtained.

The use of these numbers leads to a ratio $k_D/k_H = 0.13$ for the rates of breaking of the nitrogen-deuterium and the nitrogen-hydrogen bonds (page 81). In order for k_D/k_H to be unity or greater the experimental results would require a negative equilibrium constant for reaction (1). Hence even though the calculated value of k_D/k_H may not be numerically exact, the experimental results make it clear that nitrogen-hydrogen bonds are broken much more rapidly than nitrogen-deuterium bonds.

The competitive runs of type (2a) proceeded according to the following equations

$$OH^- + R_3SiH + PH \longrightarrow R_3SiOH + H_2 + P^-$$

and $$OH^- + R_3SiH + PD \longrightarrow R_3SiOH + HD + P^-$$

The water concentration used in these competitive hydrolyses was such that according to the kinetic evidence obtained by Dunn (7) the reaction was half order in water. Thus the proton involved in the formation of hydrogen gas would be extracted from the piperidine. The calculation of the relative rate ratio was based on the piperidine rather than the water. If this kinetic evidence is ignored and the rate ratio k_D/k_H is calculated on the basis of the proton being obtained from the water the isotope effect was in the same direction but of reduced magnitude ($k_D/k_H = .33$).

The competitive runs of type (2b) proceeded according to the following equations

$$OH^- + R_3SiD + PH \longrightarrow R_3SiOH + DH + P^-$$

and $$OH^- + R_3SiD + PD \longrightarrow R_3SiOH + D_2 + P^-$$

In order to calculate the rate ratio for this competitive type, the percent deuterium oxide had to be first corrected for the deuterium evolved by the triphenylsilane-<u>d</u>. This correction was obtained from the percent completion of the reaction.

The relative rate ratios for the various competitive runs are listed in Table XXV.

TABLE XXV.

Rate Ratio k_D/k_H From Competitive Runs.

		REACTANTS										
Run No.	Competitive Type	Triphenylsilane (Mole)	Triphenylsilane-*d* (Mole)	Toluene (Mole)	Piperidine (Mole)	Water (Mole)	Deuterium Oxide (Mole)	Percent Deuterium Oxide.	A^a	X^a	P^a	Ratio k_D/k_H.
13	1a	.001923	.001915	.1874	.406	.1102		1.542	.842	.630	.4560	.67 ± .02
14	1a	.001923	.001915	.1874	.406	.1102		1.410	.842	.621	.4107	.68 ± .02
10	2a	.001923		.0937	.203		.0552	1.118	2.684	.365	.00907	.13 ± .02
11	2a	.001923		.0937	.203		.0552	.571	2.684	.320	.00505	.12 ± .02
12	2a	.001923		.0937	.203		.0552	.783	2.684	.342	.00685	.13 ± .02
15	2b		.001915	.0937	.203		.0552	4.992	2.684	.292	.00824	.10 ± .02
16	2b		.001915	.0937	.203		.0552	1.235	2.684	.279	.00226	.10 ± .02

[a] A, X and P are the ratios as defined on page 76.

DISCUSSION

The rate ratio k_D/k_H for the silicon-hydrogen bond breaking obtained from the kinetic and the competitive hydrolyses, 0.72 and 0.68, respectively, are in good agreement and show that the results of Gilman, Dunn and Hammond (12), (k_D/k_H approximately equal to 6) were in error. The error could possibly be due to the presence of impurities in either of the silanes used[5]. The slight discrepancy from Wilzbach and Kaplan's value of $k_D/k_H = 0.9$ is to be expected in that different methods were employed in obtaining the rate ratio.

These new results, however, fail to answer the question of whether the silicon-hydrogen bond breaking is part of the rate-determining process. The observed isotope effect is small, which could mean that the breaking of the silicon-hydrogen bond is not involved in the rate process. It could also mean that the bond breaking is involved but that the hydrolysis proceeds through a tightly bonded intermediate as proposed by Gilman, Dunn and Hammond (12). In the latter case the partial formation of the hydrogen-hydrogen bond in the transition state could nearly cancel the normal isotope effect. The results therefore do not distinguish between these two cases.

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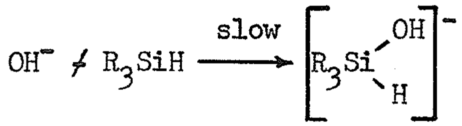
[5] It may be seen that not too much reliance should be placed on individual reaction rates in silane hydrolyses from the fact that the initial rate in competitive reactions of triphenylsilane and triphenylsilane-d̲ and between piperidine and piperidine-d̲ were greater in both cases than any of the rates when carried out separately.

If the silicon-hydrogen bond breaking is involved in the rate process the mechanism could be

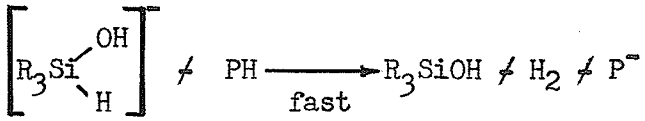
$$OH^- + R_3SiH \xrightarrow{slow} R_3SiOH + H^-$$

$$H^- + PH \xrightarrow[fast]{} P^- + H_2$$

or



$$OH^- + R_3SiH \xrightarrow{slow} \left[R_3Si\begin{matrix}OH\\H\end{matrix}\right]^-$$



$$\left[R_3Si\begin{matrix}OH\\H\end{matrix}\right]^- + PH \xrightarrow[fast]{} R_3SiOH + H_2 + P^-$$

The large isotope effect obtained in the formation of hydrogen is proof that the breaking of the nitrogen-hydrogen bond in piperidine is one of the governing factors in the second step by either mechanism. The same would be also true for the mechanism proposed by Gilman, Dunn and Hammond (12), (page 18).

By the mechanism of Gilman, Dunn and Hammond (12) the small isotope effect in silicon-hydrogen bond breaking would be due to the tightness of the bonding in the transition state. This tight bonding in the transition state might also be expected to result in a small isotope effect for nitrogen-hydrogen bond breaking. Since the isotope effect for nitrogen-hydrogen bond breaking has been shown to be large, the results of the present investigation would seem to favor the two-step mechanism.

CONCLUSIONS

(1). The relative rates of hydrolysis of triphenylsilane-d and triphenylsilane were determined by competitive hydrolysis as well as by kinetic rate ratios.

The rate ratio k_D/k_H as calculated from kinetic runs was:- $0.73 \pm .04$ when carried out employing the piperidine-water solution as hydrolyzing agent and $0.71 \pm .04$ when carried out in piperidine-deuterium oxide solution. The rate ratio k_D/k_H as calculated from competitive hydrolysis was:- $0.68 \pm .02$.

The results of the two methods were in agreement to within the experimental error and comparable to the results obtained by Wilzbach and Kaplan (28). However the isotope effect is of such a small magnitude that the question of whether or not the breaking of the silicon-hydrogen bond is involved in the rate controlling process remains unsettled.

(2). The relative rates of proton uptake were determined and k_D/k_H was found to be $0.13 \pm .02$ taking the proton to be obtained from piperidine. This isotope effect proves conclusively that the breaking of the nitrogen-hydrogen bond is involved in the rate of proton abstraction.

(3). Finally, the results obtained favor a two step mechanism for the hydrolysis of triphenylsilane.

RECOMMENDATIONS FOR FUTURE INVESTIGATION

The results of this investigation failed to prove whether or not the breaking of the silicon-hydrogen bond is involved in the rate controlling process. Further, it did not prove conclusively that the reaction proceeds through a two step mechanism.

These queries could be answered by determining the order of all the reactants in a single aprotic medium. For example, if the reaction could be shown kinetically to be first order in proton donor as well as in the base, it would be certain that silicon-hydrogen bond breaking is part of the rate determining process.

Should this be true, the hydrolysis of silanes would be the first established case where isotopic bond breaking in the rate determing step does not produce a definite isotope effect.

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