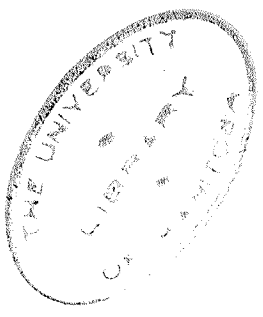
THE KINETICS AND MECHANISM OF THE HYDROLYSIS OF TRIPHENYLSILANE

by

Carl Brynko.

A Thesis Submitted to the
Faculty of Graduate Study and Research
Of the University of Manitoba
In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy.

February 1956.



ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. G. E. Dunn who through his advice, guidance and many stimulating discussions made the present investigation not only interesting but also enjoyable.

Thanks are also due to the National Research Council for two Summer Grants.

The Kinetics and Mechanism of the Hydrolysis of Triphenylsilane.

Abstract.

The hydrolysis of triphenylsilane in wet piperidine which can be represented as

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

was investigated kinetically. The following rate expression for this hydrolysis when carried out in toluene was derived experimentally:

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

where SH represents triphenylsilane and PH represents piperidine. This rate expression was found to be valid through a range of water concentrations from .15 to 14.82 molar. The above kinetics showed that previously proposed mechanisms were inadequate and the following mechanism was proposed

$$R_3SiH + C_5H_{10}NH \overset{\text{Fast}}{\rightleftharpoons} R_3\overset{H}{\underset{|}{Si}}.\overset{H}{\underset{|}{N}}C_5H_{10}$$

$$OH^- + R_3\overset{H}{\underset{|}{Si}}.\overset{H}{\underset{|}{N}}C_5H_{10} \overset{\text{Slow}}{\longrightarrow} R_3SiOH + H_2 + C_5H_{10}N^-.$$

Kinetic and isotopic evidence dictated that the above mechanism proceed through a tightly bonded transition state as proposed by Gilman, Dunn and Hammond (17). Further kinetic evidence was obtained which indicated that in a strongly polar solvent medium the reaction proceeds by a different mechanism, although the kinetics were not completely solved.

A new method for preparing N-alkyl piperidines in good yields has been evolved. This synthesis employs piperidine hydrochloride and a primary or secondary alkyl halide.

TABLE OF CONTENTS

Table of Contents (Cont.)

LIST OF TABLES

List of Tables (Cont.)

LIST OF FIGURES

INTRODUCTION

INTRODUCTION

The alkaline cleavage of the silicon-hydrogen bond in trialkyl- and triarylsilanes has been the subject of both kinetic and isotopic investigation. The hydrolysis of trialkylsilanes was investigated kinetically by Price (45) and the hydrolysis of triarylsilanes by Dunn (11). The results of these investigations show that the reaction can be represented stoichiometrically by the equation

$$OH^- + R_3SiH + HA \longrightarrow R_3SiOH + H_2 + A^-$$

where R represents any alkyl or aryl group and HA is a proton donor. The attack of the hydroxide ion causes the displacement of the silane hydrogen with the pair of electrons which had constituted the bond. This hydrogen because of its reactivity extracts a proton from some proton donor that is present when the displacement occurs.

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 independent kinetic runs showed that triphenylsilane-d reacted nearly six times faster than its protium analog (17).

Isotopic investigations carried out by Wilzbach and Kaplan

(32, 58) and by Dunn and Brynko (7) have shown that the abnormal isotope effect observed by Dunn was in error and that the rate ratio k_D/k_H was somewhat less than unity (0.73 to 0.8). Further, the effect of isotopic substitution in the solvent medium (which hereafter will be called the solvent isotope effect) was found by competitive methods to be large by both groups of investigators.

The results of these investigations, however, failed to clearly establish the mechanism of the hydrolysis of tri-substituted silanes. It has been the purpose of this investigation to attempt a clarification of the mechanism by means of a kinetic study. The order of the reaction with respect to the reactants has been determined in the two solvents, toluene and dimethylformamide. The hydrolysis has also been carried out in various solvents employing a variety of bases.

In addition to this work, the solvent isotope effect was kinetically determined for the silane hydrolysis.

HISTORICAL

HISTORICAL

The cleavage of the silicon-hydrogen bond presents a rather unique reaction which has no parallel in carbon chemistry. In the cleavage of the carbon-hydrogen bond, the hydrogen atom leaves the reaction centre without the pair of electrons which had constituted the normal bond and is thus termed a proton. On the other hand, when the silicon-hydrogen bond is cleaved the hydrogen atom leaves the reaction centre with the pair of electrons normally involved in the bond. This hydride-hydrogen with a pair of electrons has been termed a hydride ion (21), but because of its extreme reactivity its presence as a free ion in aqueous solution is doubtful.

The hydrolysis of trialkylsilane was first studied kinetically by Price (45). 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 derived from 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 a variety of alcohols and analyzing the evolved gas. Both chemical and mass spectrometric analysis showed that in all cases the gas was at least 98% hydrogen indicating the reaction proceeds according to equation (a). These results also supported the view that the cleavage of the silicon-hydrogen bond was of the hydride ion type and did not correspond to the carbon-hydrogen cleavage which involves the cleavage of a proton.

The hydrolysis of diethylmethylsilane was chosen for a study of the kinetics. The rate of hydrogen formation was followed volumetrically and to insure a smooth evolution of gas it was found necessary to shake the reaction vessel. The order with respect to silane was determined by variation of the silane concentration and was found to be first order. When all the reactants but silane were present in excess the hydrolyses followed pseudo-first order kinetics to approximately 80% completion, further substantiating the first order in silane. Similarly, by varying the hydroxide ion concentration the hydrolysis was found to be first order with respect to this reactant.

Since the reaction was carried out in aqueous alcohol medium the role of the water and alcohol was also investigated. The reaction was found to proceed in anhydrous alcohol but its order was

not determined. The reaction was found to be first order with respect to water by varying the water concentration from 3 to 19 molar in an alcoholic medium. This indicated that both water and the alcohol acted as proton donors in the hydrolysis and the rate constant could be written in the form

$$k = a + b\,[H_2O]$$

where k = observed rate constant; a = the constant for the dependence of the rate on the alcohol concentration; and b = the constant for the water dependence of the reaction.

The results of a kinetic study involving a series of mixed alkyl substituents in the trialkylsilane showed that as the size and complexity of the substituents increased, the rate of hydrolyses decreased. This behavior was in accordance with the results generally observed in nucleophilic displacements in carbon chemistry. Subsequent investigations carried out with various silanes have also borne out this similarity of structural effects (19, 20, 44, 54, 57).

A kinetic investigation of the mechanism of triarylsilane hydrolysis was carried out by Dunn (11). 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 (33). The reaction was found to be pseudo-first order with respect to 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 with respect to water up to concentrations of 2 molar. The half-order with respect to the water concentration was explained by the following relations. Price in his investigation had shown that the reaction was first order with respect to both silane and hydroxide ion. Therefore the rate of disappearance of silane could be expressed as

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

where SH represents silane.

The half-order in water suggested that the hydroxide ion was the attacking species in this reaction also. The hydrolyzing solution could equilibrate according to the following equation

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

where PH represents piperidine,

and then

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

If P was set equal to the initial concentration of PH; W equal to

the initial concentration of H_2O; and x equal to the equilibrium concentration of PH_2^+ ; then x is also equal to the OH^- concentration and the equilibrium equation became

$$\frac{x^2}{(P-x)\ (W-x)} = K$$

Since P and $W \gg x$ (Piperidine is a weak base $K_B = 1.35 \times 10^{-3}$)

$$\frac{x^2}{PW} \cong K$$

then $x^2 \cong KPW$ or $x = K^{\frac{1}{2}}P^{\frac{1}{2}}W^{\frac{1}{2}}$

and therefore

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

The hydrolysis is first order with respect to silane, and if it is also first order with respect to hydroxide ion, then

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

$$= kK^{\frac{1}{2}} [SH][PH]^{\frac{1}{2}} [H_2O]^{\frac{1}{2}}$$

This treatment accounted for the observed half-order with respect to water; however, if the hydroxide ion was the attacking species, the source of the second hydrogen atom involved in the production of the hydrogen molecule was unaccounted for. To account for this 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

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

Of course the three-halves order with respect to piperidine could not be observed since piperidine was the solvent. A proton should be more easily obtained from the water, and as the water concentration increases this should increase the order with respect to water,

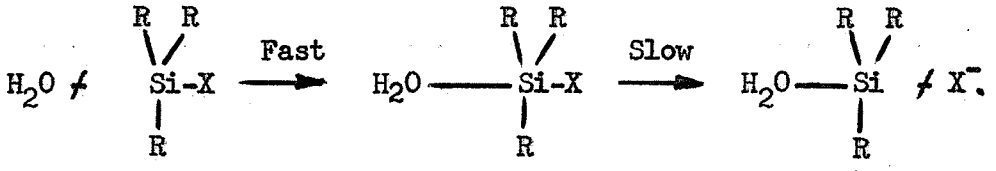
$$OH^- + SH + H_2O \longrightarrow SOH + H_2 + OH^-.$$

The rate expression then became

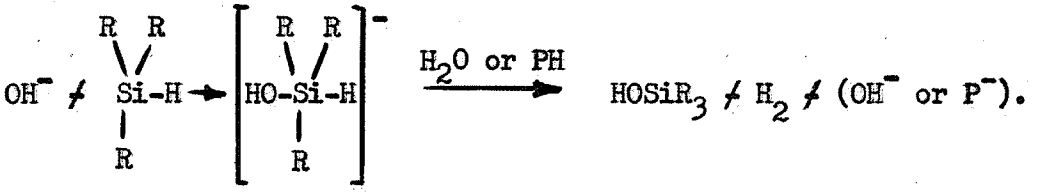
$$-\frac{d[SH]}{dt} = kK^{\frac{1}{2}} [SH][PH]^{\frac{1}{2}} [H_2O]^{3/2}.$$

The three-halves order with respect to water was not realized because at higher water concentrations the reaction solution did not remain homogeneous.

The above interpretation of the reaction was very similar to that developed by Price for the hydrolysis of trialkylsilanes. However, in a kinetic investigation (53) involving the hydrolysis of triarylhalosilanes by water, Swain suggested that a pentacovalent intermediate was involved in the mechanism, and could be illustrated as



The hydrolysis of triarylsilanes could similarly be represented by the equation



The next problem was to determine whether the first or the second step was fast. If the first is fast and the second is slow, then the overall order of the reaction would be given by the expression

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

in piperidine, or

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

in a non-participating solvent. If the first step is slow and the second fast, then in any medium in which water concentration exceeds the silane concentration ten to one or more, the water consumed in the second step would not appear in the rate, and the equation would become

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

This question could be answered if the order of the reaction with respect to all three reagents, piperidine, water and silane could be determined in a single medium. Methyl cellosolve was chosen as the solvent and the results showed that the reaction was half-order with respect to piperidine, but zero order with respect to water at low water concentrations. The zero order with respect to water was taken to show that methyl cellosolve replaced water in the preliminary equilibrium with piperidine

$$CH_3OCH_2CH_2OH + PH \overset{K}{\rightleftharpoons} CH_3OCH_2CH_2O^- + PH_2^+$$

If this were true then the attacking species would be the 2-methoxyethoxide ion instead of the hydroxide 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 re-

action 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 appeared to be the hydroxide 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 appeared to be the 2-methoxyethoxide ion which is a stronger nucleophilic reagent than the hydroxide 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 was 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 an isotopic study was undertaken. Triphenylsilane-d was prepared and its rate of hydrolysis checked against that of the normal silane. The isotopic method of determining whether or not the breaking of a bond to hydrogen is concerned in the rate controlling step of a reaction has been fairly widely applied in the cleavage of carbon-hydrogen bonds (39, 43, 50, 56) but this was the first case where it had been applied to a reaction in which silicon-hydrogen bond fission would lead to the formation of a hydride ion. In

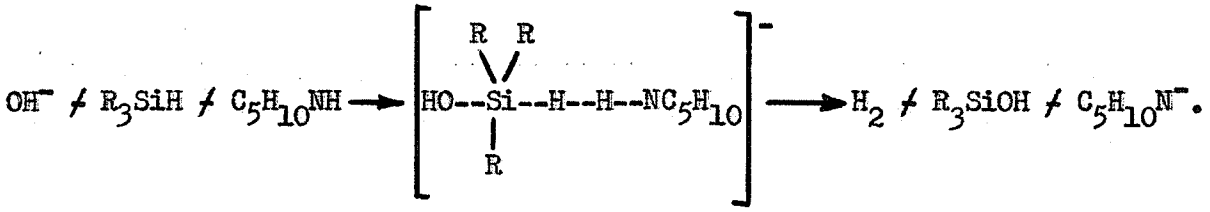
general, where the breaking of a bond to hydrogen is involved in the rate controlling step, the reaction is slower with the compound containing deuterium than with the one containing protium. When the breaking of a bond to hydrogen is not rate controlling the rate is essentially the same in both cases. The difference in rate with the two isotopes is due to the fact that the mass ratio between deuterium and protium is large for isotopes and, consequently, the difference in zero point energy between compounds containing these isotopes is significantly large. Since deuterium is heavier than protium the fundamental vibration frequency, and therefore the zero point energy, of deuterium compounds will be smaller than those of protium compounds. As the molecules move from their ground state into a transition state there is a general loosening of the bonds at the point of attack, with consequent decrease in vibration frequencies and zero point energies. Since protium compounds have larger zero point energies than deuterium compounds in the ground state, a proportional decrease in zero point energies will give a larger absolute decrease for the protium than for the deuterium analog. Consequently, the activation energy will be smaller, and the rate of reaction faster, for the protium compound than for the deuterium one.

The results of the isotopic investigation carried out by Dunn showed that triphenylsilane-d hydrolyzed six times faster than did triphenylsilane. This indicated that, contrary to the considerations outlined above, the breaking of the silicon-hydrogen bond was

part of the rate controlling process. However, the sign of the isotope effect was opposite to that expected on the basis of bond rupture involving isotopic species.

These results were interpreted by Gilman, Dunn and Hammond in the following manner. It was 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 state of the reactants.

While the lack of a detailed knowledge of the configuration of the transition state for the hydrolysis of triphenylsilane did not permit a complete interpretation of the observed results, it seemed likely that the abnormal effect should be attributed in large part to the fact that the reaction effectively involved the displacement of a hydride ion. Because of the rather low electron affinity of hydrogen atoms [17 kcal. per mole (23)] such a displacement would not be expected to occur at ordinary temperatures unless the hydrogen was 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



Where the dotted bonds in the transition state represent the partially destroyed bond between silicon and hydrogen as well as that between nitrogen and hydrogen and the newly formed bond between the hydrogen atoms.

Since the hydrogen-hydrogen bond has a rather large stretching force constant [5.76×10^5 dynes per cm. (29)] the restoring force for vibrational displacement of the hydrogen atom might well be larger in the transition state than in 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-hydrogen were investigated by Wilzbach and Kaplan (58). 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 rates of hydrolysis (ratio of k_T/k_H) was 0.7. The results of the hydrolyses of lithium aluminum hydride and lithium borohydride were not precisely reproducible, falling in the range of 1.2 to 0.8 (59, 60).

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 analysis 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, 13).

An isotopic investigation of triphenylsilane hydrolyses was undertaken by Dunn and Brynko (7) employing both kinetic and competitive hydrolyses. The kinetic isotope effect for the breaking of the silicon-hydrogen bond was determined by comparing the rates of hydrolyses of triphenylsilane-d and triphenylsilane. The rate ratio k_D/k_H was found to be 0.72. In the competitive hydrolyses, an equal mole ratio of triphenylsilane-d and triphenylsilane was reacted competitively in the same reaction medium. The hydrolyses were stopped at approximately 50% completion and the evolved gas, consisting of a mixture H_2 and HD, was oxidized to water. The water samples were purified and analyzed for deuterium by the gradient density tube method (1). The rate ratio k_D/k_H was calculated from the percent deuterium in the water sample and found to be 0.68.

The agreement between the kinetic and competitive isotope effects was good in this investigation and these results were likewise in good agreement with those of Wilzbach and Kaplan (58), considering that the results were obtained by different methods.

In addition, the hydrolysis of triphenylsilane was carried out in a piperidine-deuterium oxide solution to determine if the substitution of hydrogen by deuterium in the solvent had any effect on the reaction. The competitive rate ratio k_D/k_H for proton uptake calculated on the assumption that piperidine donated the proton was 0.13, and 0.34 if the proton was obtained from water.

A clear distinction should be drawn between a kinetic and a competitive isotope effect. A kinetic isotope effect will occur when there is a choice between protium and deuterium in the step that controls the rate of appearance of the products or any step that precedes it. A competitive isotope effect will be observed where there is a choice between protium and deuterium in the step that produces the products or any step that precedes it.

The following mechanisms would be in agreement with the established kinetic evidence.

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

(b) $OH^- + R_3SiH \xrightarrow{\text{Slow}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

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

(c) $OH^- + R_3SiH \xrightarrow{\text{Fast}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

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

It will be noted that in all three mechanisms (a), (b), and (c) there is a choice between protium and deuterium in the formation of products and a competitive isotope effect should be observed in all three mechanisms. Consequently the competitive solvent isotope effect observed by Dunn and Brynko did not distinguish among the three mechanisms. A choice is offered in the step that determines the rate in mechanisms (a) and (c) but not in (b). However, no attempt was made to determine the kinetic solvent isotope effect.

The isotope effects observed in this investigation also failed to answer the question of whether the silicon-hydrogen bond

breaking was part of the rate-determining process. Both the kinetic and competitive isotope effects in the cleavage of the silicon-hydrogen bond were small, which could mean that the breaking of the silicon-hydrogen bond is not involved in the rate-controlling process. It could also mean that bond breaking is involved but that the hydrolyses proceed through a tightly bonded intermediate as proposed by Gilman, Dunn and Hammond (17). 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 did not distinguish between these two cases.

However, if a tightly bonded intermediate produced a small silicon-hydrogen isotope effect it was thought that the solvent isotope effect should be small also. Since the competitive isotope effect for solvent-hydrogen bond breaking had been shown to be large, the results of this investigation were taken to favor the two-step mechanisms.

Wilzbach and Kaplan (32) extended their original investigation by determining the competitive solvent isotope effect in both triphenylsilane and tripropylsilane hydrolysis employing deuterium and tritium. These authors calculated the solvent isotope effect on the assumption that the proton was obtained from water whereas Dunn and Brynko assumed that the proton came from piperidine. The results of these two investigations were in excellent agreement if the calculations were based on the same proton source.

Wilzbach and Kaplan, however, went a step further and determined the solvent isotope effect in two isotopically substituted media, piperidine water and aqueous alcohol. They observed that the competitive isotope effect in the aqueous alcohol solvent was considerably larger than that in the piperidine-water solvent. These results, the investigators concluded, favored the concerted or one step mechanism (a) below,

$$R_3SiH + OH^- + HA \longrightarrow R_3SiOH + H_2 + A^- \qquad (a)$$

rather than the two step mechanism (b)

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

$$\left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^- + HA \xrightarrow{\text{Fast}} R_3SiOH + H_2 + A^- \qquad (b)$$

where HA represents the solvent. These correspond to the mechanisms (a) and (b) proposed by Brynko, page 16. The rather large change in the isotopic rate ratio for triphenylsilane upon changing the solvent from piperidine-water to ethanol-water was taken to be a strong argument in favor of mechanism (a) since it implied considerable interaction in the transition state between the silane hydrogen and the solvent. They also observed a greater kinetic rate of hydrolysis

of tripropylsilane in ordinary alcohol-water solvent than in the deuterated solvent, thus showing that the solvent participates in the rate-determining step. This again favored the concerted mechanism (a) as opposed to the two step mechanism (b).

Apparently Wilzbach and Kaplan had overlooked the possibility of yet a third mechanism which their kinetic solvent isotope effect admitted

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

$$\left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^- + HA \xrightarrow{\text{Slow}} R_3SiOH + H_2 + A^-$$

where HA represents solvent. This would correspond to mechanism (c), page 16. The kinetic solvent isotope effect indicated that the process of proton abstraction was involved in the rate controlling step and the above mechanism was therefore consistent with this fact. Perhaps this mechanism was disregarded because these investigators calculated the isotope effect on the basis of water as the proton donor which in this third mechanism would require the order with respect to water to be three-halves. The order with respect to water had been observed by Dunn to be one-half. However, if the possibility that piperidine is the proton donor is admitted the

third mechanism was in agreement with the data.

From the above survey of the work carried out toward establishing the mechanism for the hydrolysis of silanes it can readily be seen that the mechanism had not been established with certainty. The purpose of the present investigation was to study the mechanism further by carrying out a more thorough kinetic investigation.

KINETIC RESULTS AND DISCUSSION

KINETIC RESULTS AND DISCUSSION

To summarize the work of previous investigations into the hydrolysis of triphenylsilane by aqueous piperidine the following points of information were available:

(1) the reaction was first order with respect to silane;

(2) the reaction was half-order with respect to water;

(3) kinetic isotope effect for cleavage of silicon-hydrogen bond was 0.72;

(4) competitive isotope effect for the cleavage of silicon-hydrogen bond was 0.68 to 0.80;

(5) competitive isotope effect for the cleavage of solvent bond in formation of hydrogen was large.

The various mechanisms which have been postulated are

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

(b) $OH^- + R_3SiH \xrightarrow{\text{Slow}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

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

(c) $OH^- + R_3SiH \xrightarrow{\text{Fast}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

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

where PH represents piperidine.

Another mechanism can be added in which the proton donor is water as postulated by Wilzbach and Kaplan,

(d) $OH^- + R_3SiH \xrightarrow{\text{Slow}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

$$\left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^- + H_2O \xrightarrow{\text{Fast}} R_3SiOH + H_2 + OH^-$$

These mechanisms which have been postulated in previous investigations assume that either water or piperidine is the proton donor. It may be noted that in a piperidine-water mixture another possible proton donor, piperidinium ion, is present. Hence a fifth mechanism which would fit all the data available at this point is as follows.

(e) $OH^- + R_3SiH \xrightarrow{\text{Slow}} \left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^-$

$$\left[R_3Si\begin{matrix}H\\OH\end{matrix}\right]^- + PH_2^+ \xrightarrow{\text{Fast}} R_3SiOH + H_2 + PH$$

A mechanism resembling (e) in which the second step is slow is ruled out because the order with respect to water would be first, whereas it has been shown to be one-half. Yet another mechanism in which water is the proton donor and resembling mechanism (d) but having the second step slow must also be discarded because this mechanism would require three-halves order with respect to water.

The kinetic expressions for the remaining mechanisms, (a), (b), (c), (d) and (e), can be obtained in the following manner. Previous investigations have indicated that the hydroxide ion is the attacking species formed by a preliminary equilibrium

$$C_5H_{10}NH + H_2O \overset{K}{\rightleftharpoons} OH^- + C_5H_{10}NH_2^+.$$

and $[OH^-]$ has been shown to be proportional to $[PH]^{1/2}\,[H_2O]^{1/2}$. For the mechanisms in which the second step is fast the rate expression would be of the form

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

where SH represents silane and PH piperidine. This rate expression would be consistent with mechanisms (b), (d) and (e). The mechanisms (a) and (c) require that the proton donor be included in the kinetics, giving the rate expression

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

Consequently a kinetic study in which the order of the reaction with respect to piperidine was determined would distinguish between the two groups of mechanisms.

The Kinetic Order of the Reactants in Toluene.

In the kinetic study carried out by Dunn the triphenylsilane was hydrolyzed by a piperidine-water solution. However, to determine the order with respect to both piperidine and water the reaction would have to be carried out in an inert solvent. In the present investigation toluene was chosen as the solvent. It has been previously shown that the products of the reaction employing a piperidine-water solution were triphenylsilanol and hydrogen. These products were also isolated in this investigation when toluene was added to the reaction solution.

Effect of Varying the Piperidine Concentration.

The order with respect to piperidine for triphenylsilane hydrolysis in toluene was determined by carrying out two series of runs in which the piperidine concentration was varied. In one series, the water concentration was fixed at 1.86 molar and the piperidine concentration varied from 3 to 6 molar. The total volume was maintained at 15 ml. by varying the toluene concentration. In the second series, the water concentration was fixed at 5.21 molar and the piperidine concentration varied in the same range of

concentrations as the first series. The data for these runs can be seen in Table I and the graphical plot of the rate constants vs. the three-halves power of piperidine in Figure 1.

The kinetic expressions for the hydrolysis given on pages 24 and 25 indicate that the order with respect to piperidine might have the values one-half and three-halves. The results of Figure 1 definitely establish this as three-halves. This shows piperidine is the proton donor and therefore eliminates all the mechanisms but (a) and (c).

TABLE I.

Rate Constants for Kinetic Runs in Which Piperidine Concentration was Varied

(A) Water Kept Constant at 1.86 Molar.

Run No.	Piperidine concentration	$PH^{3/2}$	$PH^{3/2} \times H_2O^{1/2}$	Rate Constant $\times 10^4$.
38	3.39	6.24	7.88	0.45
39	4.73	10.30	14.00	0.77
40	6.42	16.24	21.81	1.20

(B) Water Kept Constant at 5.21 Molar.

41	3.29	5.97	13.00	0.49
42	3.95	7.85	17.07	0.75
43	4.60	9.87	22.50	1.06
44	5.26	12.07	27.27	1.37
45	5.81	14.00	33.75	1.77

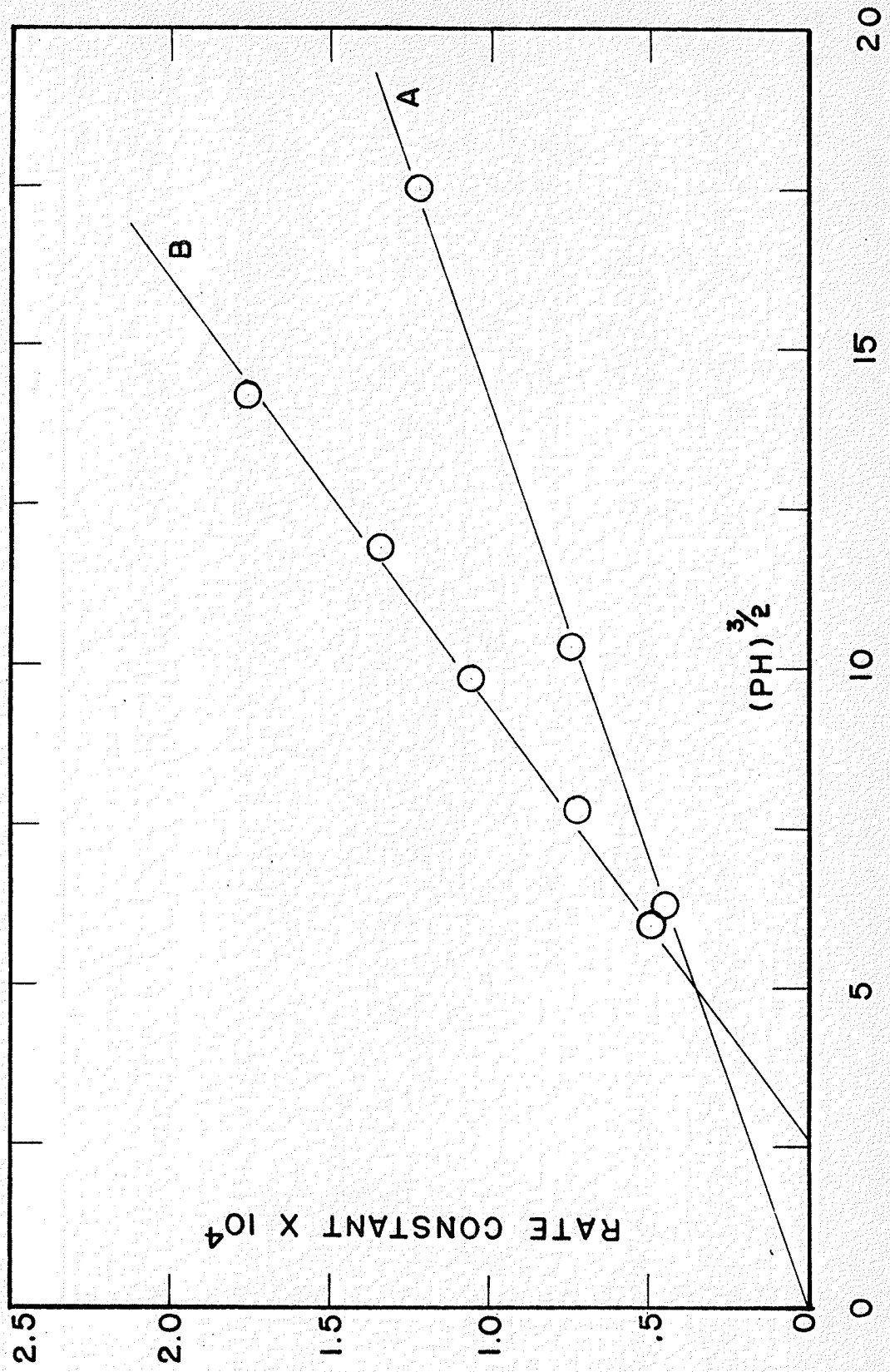


Fig. 1. Relationship between rate constant and three-halves power of the piperidine concentration. A. Water constant at 1.86 molar. B. Water constant at 5.21 molar.

Effect of Varying the Water Concentration.

It is not surprising that piperidinium ion is not the proton donor since it is formed in the preliminary equilibrium and would be present in an extremely small concentration. But it is surprising that piperidine should hold that position instead of water which is a weaker base and should therefore be a much better proton donor. This can possibly be due to the fact that the water concentration was low and the piperidine, because of its greater concentration, was favored in that role. It would be expected that at the higher water concentrations where the piperidine concentration is considerably lower than that of water, the role of proton donor would be taken over by water. In terms of mechanisms, (c) would gradually yield to mechanism (d) as the water concentration surpassed that of piperidine. Dunn in his investigation was unable to attain high water concentrations using a piperidine-water solution because it failed to dissolve the triphenylsilane at water concentrations beyond 2 molar. It was found in this investigation that employing a hydrolyzing solution of 1 part of toluene to 2 parts of the piperidine-water mixture, water concentrations approaching 15 molar could be employed.

Kinetic runs were carried out in which the water concentration was varied from .15 to 14.82 molar in three series of runs of varying piperidine concentrations. In series 1 the total volume was fixed at 15 ml., the toluene concentration fixed at

3.11 molar and as the water concentration was increased the piperidine concentration was decreased. In series 2 the total volume was maintained at 15 ml., the piperidine concentration was fixed at 6.09 and with increasing water concentration the toluene concentration was decreased. A third series of runs was carried out in which the piperidine concentration was maintained intermediate to series 1 and 2. The results of these three series of runs are shown in Tables II, III, and IV. The plots of the rate constant vs. the half power of water concentration are shown in Figure 2, and Figure 3 shows the rate constant vs. the water concentration. The series 1, 2 and 3 are the curves A, B and C, respectively. The plots in Figure 2 produced a linear relationship indicating that the reaction is half order with respect to water throughout the range of water concentrations studied. The slopes of the linear plots from the various series differed, indicating that the reaction is also strongly dependent on the piperidine concentration. This strong dependence has been shown in Figure 1 to be three-halves order with respect to piperidine. The rate expression for the hydrolysis of triphenylsilane in toluene by a piperidine-water solution can therefore be represented as

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

The validity of this expression was tested by a graphical plot of the rate constant vs. the product of the reactant concentration

TABLE II.

Rate Constants for Triphenylsilane Hydrolysis in Toluene.

Series 1.

Run No.	Water conc.	Piperidine conc.	Product of $(PH)^{3/2}(H_2O)^{1/2}$	Rate Constant x 10^4
1	.15	6.74	7.08	.30
2	.30	6.71	9.73	.38
3	.60	6.65	13.04	.70
4	.81	6.61	15.29	.76
5	1.26	6.53	18.97	.96
6	1.60	6.47	20.70	1.12
7	1.81	6.42	21.83	1.22
8	3.06	6.20	27.00	1.55
9	4.60	5.92	30.81	1.78
10	5.21	5.81	31.92	1.86
11	7.10	5.46	33.97	1.76
12	7.41	5.26	32.75	1.83
13	7.41	5.26	32.75	1.77
14	8.34	5.20	33.00	1.75
15	11.10	4.58	32.63	1.73
16	11.10	4.58	32.63	1.75
17	14.82	3.92	29.81	1.60
18	14.82	3.92	29.81	1.56

Total volume and toluene were kept constant. The piperidine concentration was decreased as the water concentration was increased.

TABLE III.

Rate Constants for Triphenylsilane Hydrolysis in Toluene.

Series 2.

Run No.	Water conc.	Piperidine conc.	$(PH)^{3/2}$ $(H_2O)^{1/2}$	Rate constant x 10^4
19	3.71	6.09	29.02	1.49
20	4.68	6.05	32.14	1.78
21	6.08	6.05	36.60	1.99
22	7.41	6.09	40.90	2.32
23	7.41	6.09	40.90	2.38
24	8.33	6.09	43.17	2.52
25	9.26	6.09	45.72	2.68
26	11.10	6.09	50.08	3.05
27	11.10	6.09	50.08	3.00
28	14.83	6.09	57.90	3.50
29	12.96	6.09	53.84	3.24

Total volume and the piperidine concentration were kept constant. Water and toluene were varied to maintain constant volume of 15 ml.

TABLE IV.

Rate Constants for Triphenylsilane Hydrolysis in Toluene.

Series 3.

Run No.	Water conc.	Piperidine conc.	$(PH)^{3/2}(H_2O)^{1/2}$	Rate constant x 10^4
30	6.69	5.87	36.25	2.08
31	6.69	5.87	36.25	2.11
32	9.02	5.56	39.51	2.29
33	9.42	5.56	40.43	2.36
34	11.10	5.45	42.56	2.54
35	12.43	5.36	43.81	2.68
36	12.96	5.30	44.53	2.73
37	14.82	5.20	45.62	2.84

Volume of toluene was kept constant. Water and piperidine were varied to maintain the piperidine concentration linearly intermediate to the series 1 and 2.

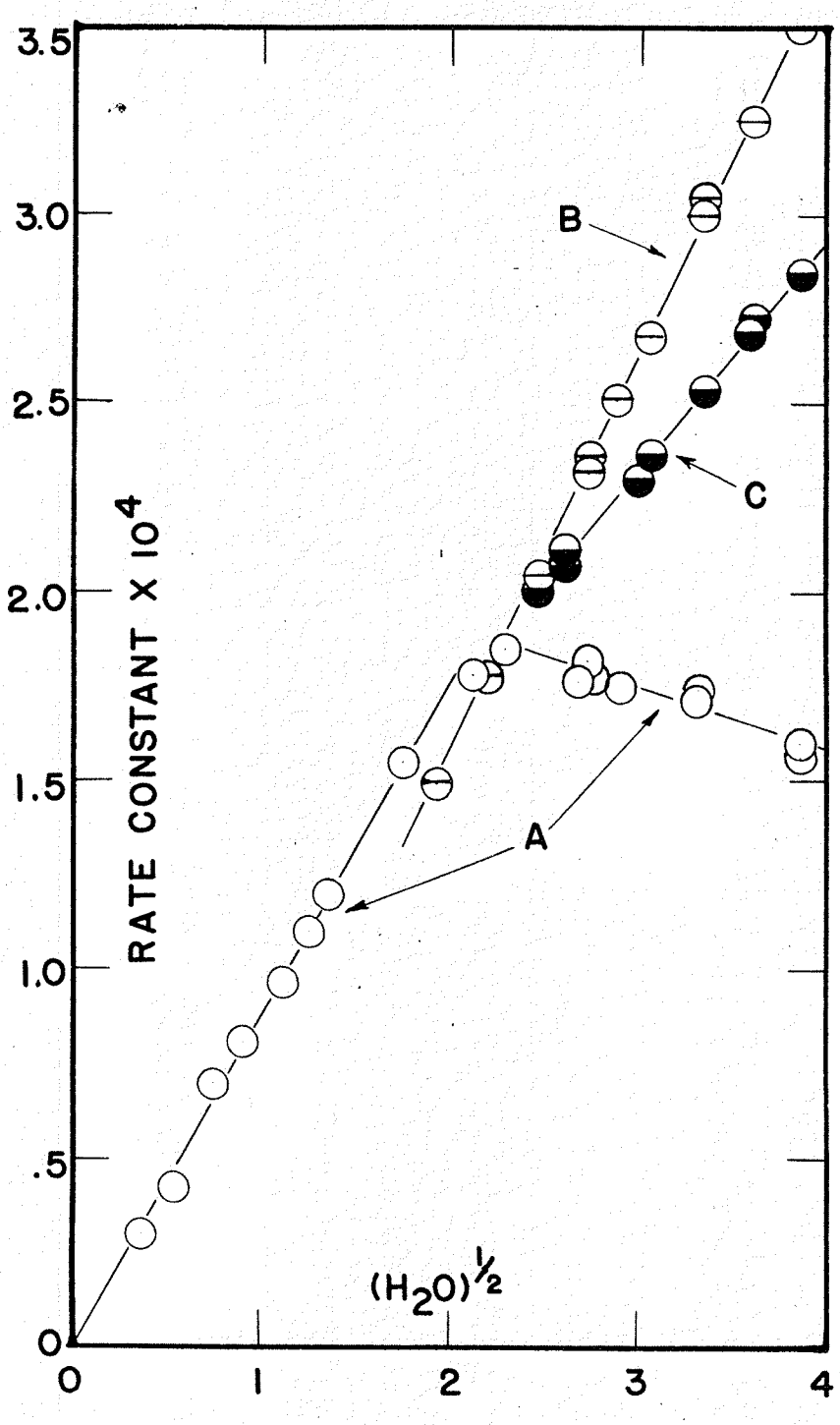


Fig. 2. Relationship between rate constants and half-power of water concentrations: ○ ○ represent series 1; ⊖ ⊖ represent series 2; and ◒ ◒ represent series 3.

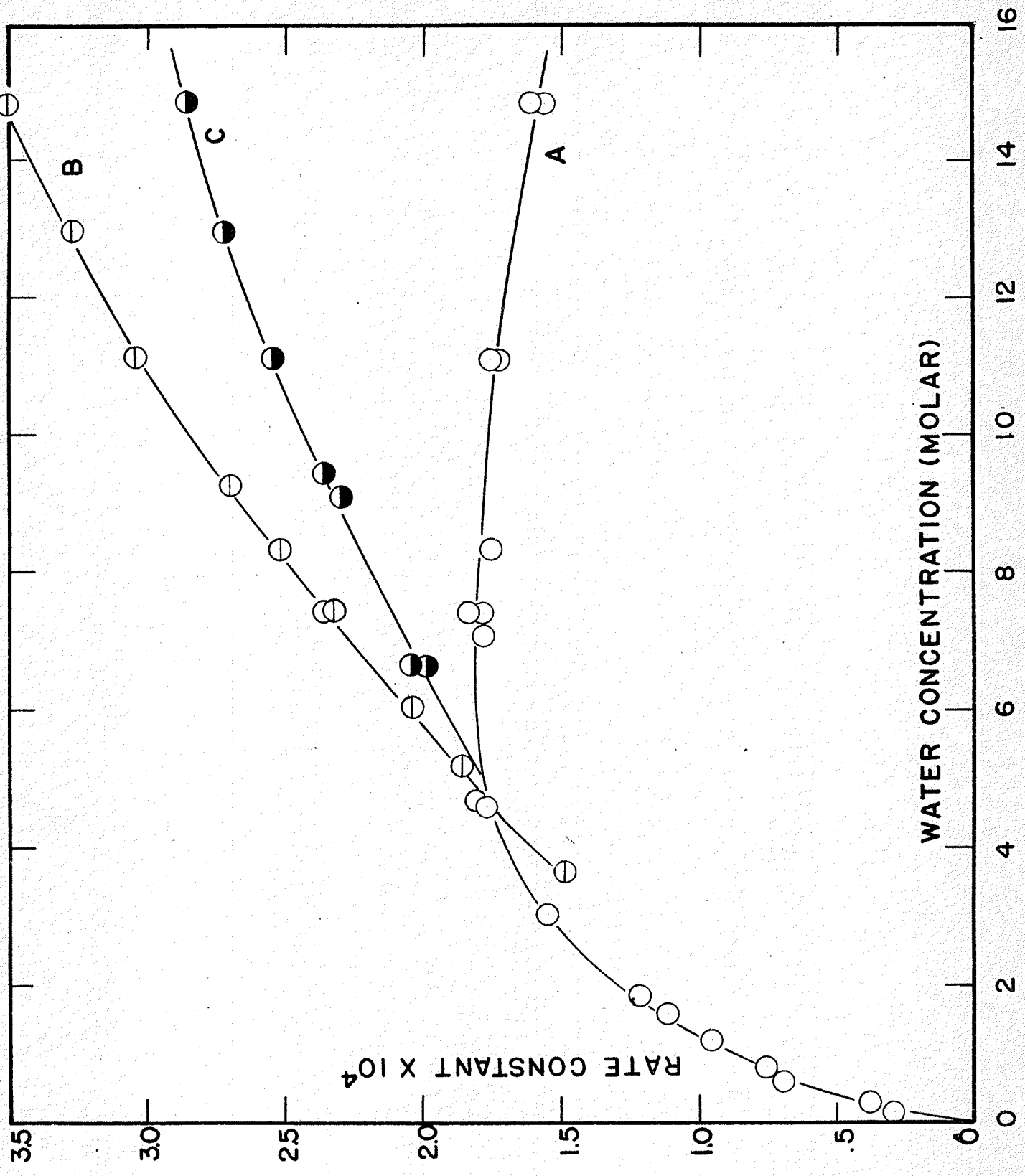


Fig. 3. Relationship between rate constant and the water concentration, symbolism is the same as in Fig. 2.

$[H_2O]^{1/2}$ $[PH]^{3/2}$ for all the runs from Tables I, II, III, and IV. The plot of these values can be seen in Figure 4. The excellent linear plot definitely establishes that the order of the reaction remained $[PH]^{3/2}$ $[H_2O]^{1/2}$ through a range of water concentrations such that the ratio OH/NH varied from .05 to 7.5.

It should be noted that the series of runs for the piperidine order at the higher concentrations (5.21 molar) presents a linear plot in Figure 4 but is displaced somewhat below the main series of runs. In Figure 1 the same series of runs failed to pass through the origin as was expected. The cause of this displacement was not obvious nor was it determined through experimentation and therefore remains unexplained.

The fact that the order with respect to water did not increase with increasing water concentrations indicated that water did not take over the role of proton donor and so the mechanism of the type (d) but in which the second step was slow can be eliminated. Since the mechanism (c) would have certainly yielded to the (d) type at higher water concentrations, the constancy of both piperidine and water orders must therefore eliminate the mechanism (c). Also mechanism (a) can be eliminated because this mechanism which is of the one step type would be dependent on the collision frequency of the reactants. Again at higher water concentrations the frequency of the water molecule collisions would require an increase in the order with respect to water.

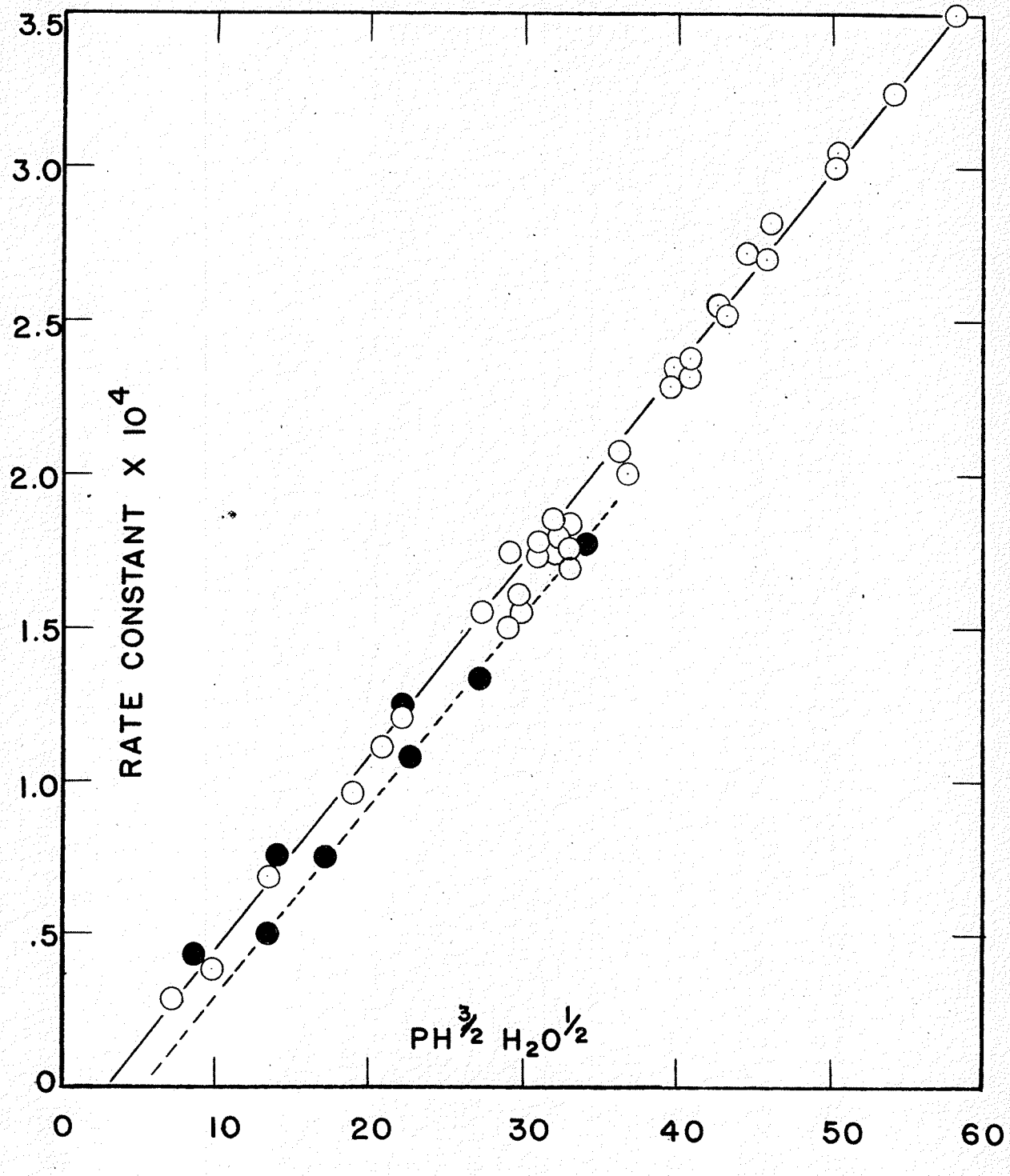


Fig. 4. Relationship between rate constant and the concentration product $[PH]^{3/2}$ $[H_2O]^{1/2}$: ○ ○ represent runs from the determination of water order; and ● ● represent runs from the determination of piperidine order.

Mechanism of Triphenylsilane Hydrolysis.

The kinetic evidence obtained in this investigation has eliminated all the mechanisms proposed on the basis of previous investigation and a new mechanism must be outlined which would be consistent with all the available evidence. The constant order with respect to piperidine through the entire range of water concentration implies that piperidine must be constrained in the role of proton donor. This could occur if the piperidine were complexed to either of the two reactants prior to the attack of the remaining one.

The most likely possibility is that piperidine should complex with water. This is suggested by the large solubility of primary and secondary amines in water and their high heat of hydration. If this complex were involved in the reaction, the following kinetics would have to apply. The complex would be formed in a preliminary reaction

$$PH + H_2O \overset{K}{\rightleftharpoons} PH.H_2O$$

It would then attack the silane molecule producing the products. If the amount of complex ($PH.H_2O$) is set equal to x the equilibrium becomes

$$K = \frac{x}{(PH-x)\ (H_2O-x)}$$

If the equilibrium constant is small so that $x \ll PH$ or H_2O then

$$K = \frac{x}{(PH)\ (H_2O)}$$

or $$x = K\ (H_2O)\ (PH)$$

The rate expression for the supposed reaction is

$$-\frac{d[SH]}{dt} = k\,[SH][x].$$

Substituting for the complex concentration, the rate expression becomes

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

which would not be consistent with the observed kinetics.

On the other hand, if the equilibrium constant is large then in the regions of low water concentration

$$x \cong H_2O$$

and the rate expression becomes

$$-\frac{d\,[SH]}{dt} = k\,[SH][H_2O]$$

or in high water concentrations

$$x \cong PH$$

and

$$-\frac{d[SH]}{dt} = k[SH][PH]$$

This implies that at either end of the water concentration range the reaction becomes independent of the piperidine or the water. Neither of these expressions fits the observed kinetics. Intermediate values of the equilibrium constant would produce intermediate kinetic expressions. Calculations of complex concentration for values of K in the intermediate ranges, failed to produce a linear plot against the rate constant.

Investigations of several workers (5, 16, 46) have shown that evidence exists for the formation of two other complexes involving piperidine and water; these are $PH.2H_2O$ and $2PH.H_2O$. However, calculations based on these two complexes have also shown that for a large range of equilibrium constants (K = .01 to 100), no plot of complex concentration vs. the rate constant produced a linear relationship. The possibility of a piperidine-water complex participation in the hydrolysis of triphenylsilane was therefore discarded.

The other possibilities of complex formation would involve silane and either water or piperidine. The formation of these complexes is not too startling in view of the fact that silicon can form hexavalent compounds through coordination with other elements or molecules. Both piperidine and water have the necessary extra

pair of electrons on the nitrogen and oxygen atoms to provide the coordination bond. If water complexes with silane to form a penta-covalent intermediate then the attack of the hydroxide ion would decompose this intermediate to form the products. The reaction should therefore be observed in the absence of the amine; that is, the reaction would be independent of the piperidine concentration. This would not be consistent with the observed kinetics.

The remaining possibility is that the silane must complex with piperidine. The formation of this complex in a rapid step followed by the hydroxide ion attack in a slow step to form the products is entirely consistent with the observed kinetics. Several investigators (22, 28, 52) have obtained evidence favoring a silane-amine complex through a nitrogen-silicon coordination bond. On the other hand, Eaborn (12) undertook a spectrophotometric investigation to determine whether this postulated complex exists in observable quantities and has shown that this is improbable, at least for SiH_4 and aromatic amines. Piper and Rochow (47) have suggested that since the only experimental evidence obtained for the complex involved halo-silanes, the isolated compounds are in reality quaternary salts of the amine employed.

The participation of this complex may be improbable but it is not impossible. The kinetic requirement for this complex is that it be formed in a rapid equilibrium process. So long as this

requirement is met the actual concentration at equilibrium may be as dictated by Eaborn's spectrophotometric study. On the above assumptions the following mechanism can be postulated

$$R_3SiH + C_5H_{10}NH \rightleftharpoons R_3Si(H)(H)NC_5H_{10}$$

$$OH^- + R_3Si(H)(H)NC_5H_{10} \xrightarrow{\text{Slow}} R_3SiOH + H_2 + C_5H_{10}N^-.$$

This mechanism would be in agreement with the observed kinetics. Further, a study of the following predictions for this mechanism can be made to determine its validity.

(a) Since the silane is attacked by the hydroxide ion the effect of more polar solvents should, according to Ingold (31) and Laidler (38), decrease the rate of reaction slightly.

(b) In the present investigation the kinetics have shown that the proton donor must be the amine; thus the reaction should go only with primary or secondary amines. Further, since triphenylsilane is in itself a bulky molecule, the primary or secondary amine must not contain large groups which could hinder or prevent the complex from forming and therefore reduce the rate of reaction.

(c) The postulated mechanism requires that the piperidine-hydrogen bond be broken in the rate controlling step (second) so that if a deuterated solvent (piperidine) is employed there should be a large kinetic solvent isotope effect.

An experimental study of these predictions was made by the methods outlined below.

Effect of Solvent Medium on the Rate of Hydrolysis. In the determination of the kinetic order with respect to piperidine and water, the reaction medium consisted of 10 ml. of hydrolyzing solution and 5 ml. of toluene. Toluene, being a non-polar solvent increased the solubility of triphenylsilane, enabling a wider range of water concentrations to be studied. The volume of toluene employed was rather small to be termed a solvent; however, increasing the volume of solvent decreased the rate considerably. The solution volume employed during the kinetic order determinations was kept constant at 15 ml., and a convenient rate of reaction was obtained by adjusting the ratios of the reactant components.

In determining the effect of the solvent medium the volume of solvent employed was increased to 10 ml. and the volume of piperidine-water solution reduced to 5 ml. The increase of solvent volume reduced the rate; however, it did approximate more closely

the normal role of a solvent.

The solvent effect was determined by employing a representative number of solvents in the dielectric constant range of 2 to 118 and included dioxane, toluene, acetone, nitrobenzene and dimethylformamide. The volume of solvent was constant but since the molecular weights and densities varied, the molarity of the solvents employed are not equal. The results of this series of runs are shown below in Table V.

TABLE V.

Effect of Solvent Medium on the Rate of Hydrolysis.

Water concentration was 1.86 molar

and piperidine concentration was 3.38 molar.

Run No.	Solvent	Molarity of Solvent	Rate Constant x 10^4
45	Dioxane	7.89	0.37
46	Toluene	6.24	0.45
47	Acetone	9.01	1.10
48	Nitrobenzene	6.49	1.36
49	Dimethylformamide	8.66	3.69

The results of Table V clearly indicate the presence of a solvent effect. The magnitude of the increase in rate with increasing polarity is small when compared to the increase in the dielectric constant in passing from toluene ($\epsilon = 2.4$) to dimethylformamide ($\epsilon = 118$). Ingold (31) has predicted that for the attack of a charged nucleophilic particle on a neutral molecule the effect of more polar medium should decrease the rate of reaction slightly. The small increase observed here is not out of line since in the solvent effects discussed by Ingold a fixed concentration of the nucleophile was employed whereas in this case the nucleophile (hydroxide ion) is produced in the equilibrium

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

The equilibrium would be expected to shift to the right in a more polar medium and the predicted small decrease could well become a small increase. The observed solvent effect is therefore consistent with the proposed mechanism.

Effect of Various Bases on the Rate of Hydrolysis. Attempts were made to determine what effect various bases had on the rate of hydrolysis. This study was concerned with base strength, type of amine, and type of alkyl substituents in the amines. Seven bases were chosen, of which three were weak and the other four were of base strength comparable to piperidine (25, 26). This series of runs was carried out employing a reaction solution 1.86 molar in water and

3.11 molar in toluene. The results along with the dissociation constants of the amines are shown in Table VI. Since each reaction was carried out in a different medium, the effective base strength need not be directly related to the dissociation constant K_B. However, it is supposed that the grosser differences in K_B would be reflected in relatively large differences in the hydroxide ion concentrations in the reaction media.

TABLE VI

Effect of Various Bases on the Rate of Hydrolysis.

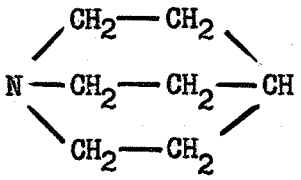
Run No.	Base	Molarity	Base Dissociation Constant K_B[a]	Rate Constant
55	Pyridine	7.87	1.61×10^{-9}	No Observable Reaction.
56	Diethanolamine	6.61	7.59×10^{-6}	No Observable Reaction.
57	Triethanolamine	5.03	6.02×10^{-7}	No Observable Reaction.
58	Diethylamine	6.49	8.91×10^{-4}	0.32×10^{-4}
59	Triethylamine	4.78	5.25×10^{-4}	No Observable Reaction.
60	N-ethyl-piperidine	4.87	2.57×10^{-4}	No Observable Reaction.
61	Di-isopropylamine	4.77	1.12×10^{-3}	2.5×10^{-6}
	Piperidine	6.42	1.35×10^{-3}	1.20×10^{-4}

[a] The K_B values for the amines were taken from one source so that all values would be comparable. (See references 25, 26.)

The results of Table VI indicate that in the weaker bases the hydrolysis is extremely slow or the reaction may not proceed at all. The slow rate of reaction in these amines can be attributed to their small base dissociation constant, which in the preliminary equilibrium would produce a correspondingly small concentration of hydroxide ion as compared to piperidine.

The absence of reaction with triethylamine and N-ethyl piperidine in spite of base strengths comparable to piperidine indicates that an amino hydrogen is involved in the production of the reaction product, hydrogen gas. The reaction with the two secondary amines diethylamine and di-isopropylamine show that indeed such is the case since both produced an observable reaction. Further, the reduced rate of reaction with di-isopropylamine as compared to diethylamine, even though the former has a larger basic dissociation constant, indicates that the isopropyl substituents must in some way hinder the rate of reaction. This observation is in good agreement with the above outlined mechanism. Considering the formation of the silane-amine complex, the two ethyl substituents in diethylamine are not as effective in shielding the nitrogen atom as are the two isopropyl substituents; thus the concentration of the silane-di-isopropylamine complex would be much smaller because of this restriction and, even though there would be a larger hydroxide ion concentration available for reaction, the reaction would proceed at a slower rate.

The reduced rate of reaction in diethylamine as compared to piperidine can also be attributed to steric requirements. In piperidine the two substituents are held rigidly, due to its cyclic structure, whereas in diethylamine the two ethyl groups are free to move and as a result would shield the nitrogen atom to a greater extent. This argument can be extended to include the tertiary amines as well where there are three substituents to shield the nitrogen and so explain the lack of hydrolyses in these amines. To determine whether the lack of the amino hydrogen or the presence of large steric effect was responsible for the absence of reaction with tertiary amines an attempt was made to use quinuclidine as the base. Quinuclidine, although a tertiary base, has a bicylic structure which leaves the nitrogen atom relatively unobstructed. Its formula is



which clearly shows the availability of the amino nitrogen. The preparation of this compound employing a five stage synthesis (See Experimental Method) yielded a small amount of quinuclidine which proved insufficient for a kinetic run. Since the preparation was lengthy and gave poor yields of the intermediate compounds the reaction with quinuclidine was abandoned.

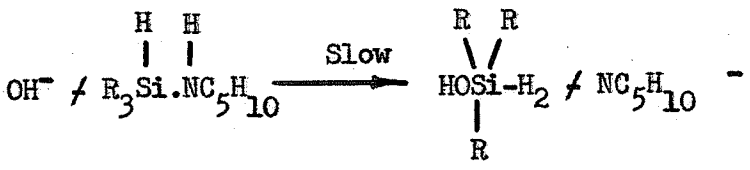
Although the role of the amino hydrogen in the formation of hydrogen gas was not conclusively proved, the experimental evidence did favor its necessity in the hydrolysis.

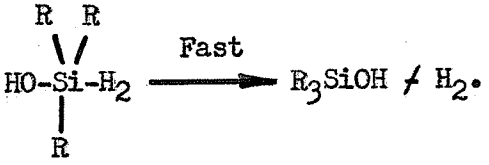
The Transition State. In a previous investigation by Dunn and Brynko (7) the isotope effects for three of the four possible combinations had been determined. The kinetic solvent isotope effect had not been calculated. The results of this isotope effect were of importance in that they would indicate whether the cleavage of the nitrogen-hydrogen bond was involved in the rate controlling step.

The determination of the kinetic solvent isotope effect was undertaken in the present investigation (See Experimental Method.). The rate ratio k_D/k_H was found to be $0.49 \pm .01$. This value was obtained from five separate runs at different reagent concentrations showing excellent agreement.

The small kinetic and competitive isotope effects (0.72 and 0.68) suggest that the cleavage of the silicon-hydrogen bond is not involved in the rate-determining process. If this is true the cleavage of this bond must occur in a rapid step following the rate-determining one. The mechanism would then have to be postulated somewhat as follows:

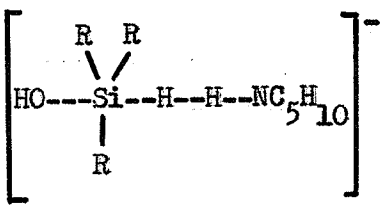
$$R_3SiH + PH \overset{K}{\rightleftharpoons} R_3\overset{H}{\underset{|}{Si}}\overset{H}{\underset{|}{.}}NC_5H_{10}$$





In this mechanism the nitrogen-hydrogen bond is broken in the rate controlling step, which precedes the product controlling step. There should be a kinetic and competitive solvent isotope effect as was in fact observed (kinetically the rate ratio k_D/k_H was 0.49 and competitively the rate ratio k_D/k_H was 0.13). However, there are difficulties involved since both the kinetic and competitive isotope effects originate in the same step, a priori they would not be expected to differ. Furthermore the structure of the short lived intermediate formed in the slow step appears highly improbable in that there is no obvious way in which the proton obtained from the piperidine can be incorporated into such a structure.

These difficulties can be resolved by postulating a process which is continuous and involves a transition state such as proposed by Gilman, Dunn and Hammond (17) and amplified by Wilzbach and Kaplan (32)



but in which the breaking of the nitrogen-hydrogen bond is still a more difficult step than the breaking of the silicon-hydrogen bond. In this transition state the following conditions would have to hold. The silicon-hydrogen bond must be nearly intact, the hydrogen-hydrogen bond very nearly formed and the nitrogen-hydrogen bond nearly broken. Then the postulated mechanism would be consistent with the kinetic and isotopic evidence.

Kinetics in Dimethylformamide.

In the study of the effect of solvent media on the rate of hydrolysis the rate in dimethylformamide was found to be large. Since dimethylformamide is an extremely polar medium it was decided to find out if this change in polarity produces any change in mechanism and whether or not the observed solvent effect was involved in the kinetics.

Effect of Varying the Water Concentration. A series of kinetic runs were carried out in dimethylformamide (DMF) which would be comparable to the series 1 in the toluene reactions. The water concentration was varied from 3 to 14.82 molar. The piperidine concentration decreased as the water concentration was increased. The DMF concentration remained fixed at 4.33 molar to maintain the 15 ml. total volume.

The results of this series of runs are tabulated in Table VII and a plot of the results is shown in Figure 5, where the rate constants were plotted against the water concentrations.

TABLE VII

Rate Constants of Silane Hydrolysis in DMF

Effect of Varying the Water Concentrations

DMF Run No.	Water Conc.	Piperidine Conc.	Rate Constant x 10^4
1	3.71	6.09	5.24
2	7.41	5.41	9.30
3	7.41	5.41	8.99
4	8.33	5.20	10.01
5	5.66	5.75	7.67
6	5.66	5.75	7.57
7	10.18	4.93	12.07
8	11.10	4.78	13.18
9	11.10	4.78	13.06
10	11.10	4.78	13.48
11	12.96	4.39	15.15
12	14.82	4.06	16.19
13	14.82	4.06	16.68

The total volume and DMF concentration were kept constant. The water and piperidine were varied to keep the total volume fixed at 15 ml.

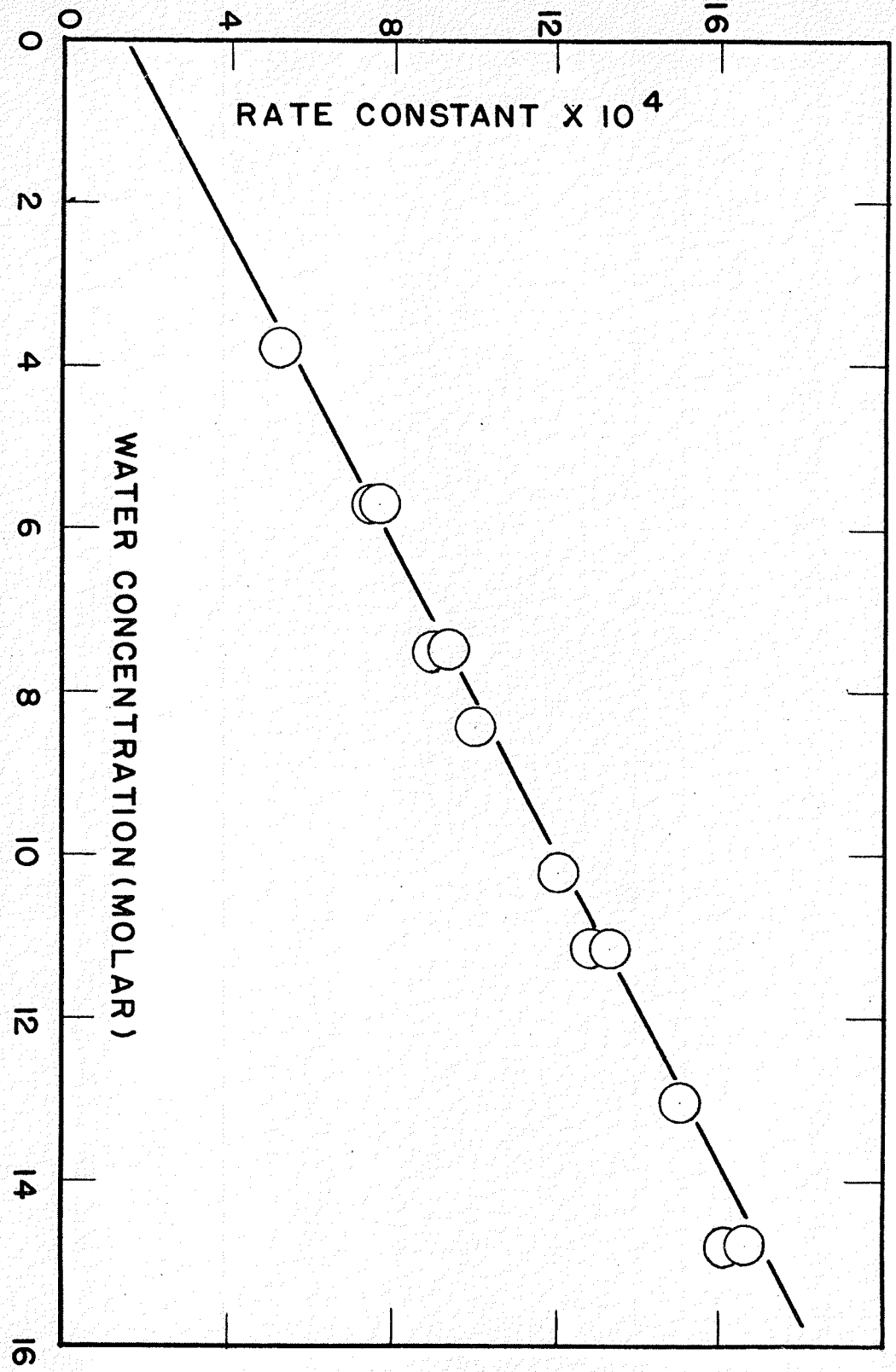


Fig. 5. Relationship between the rate constants and the water concentration.

The linear plot obtained in Figure 5 indicated that the order with respect to water was unity and the fact that the fit is good even up to 14.82 molar water suggested that the order with respect to piperidine approached zero. These results when compared to the half-order with respect to water and three-halves with respect to piperidine in toluene solution indicated that the reaction was proceeding through a different mechanism, and therefore an attempt was made to determine the order with respect to piperidine.

Effect of Varying the DMF Concentration. The kinetic order with respect to piperidine was studied by means of a series of kinetic runs carried out at a fixed water concentration of 7.41 molar. The piperidine concentration was varied in the range from 2 to 8 molar. The DMF concentrations were accordingly altered to maintain the constant volume of 15 ml. The rate constants and the corresponding reactant concentrations are shown in Table VIII while the plot of rate constant vs. the piperidine concentration is shown in Figure 6. It is evident that the data cannot be fitted to any constant power of piperidine concentration.

The dotted line of Figure 6 corresponds to the piperidine concentration used in the water variable series of Figure 5. Figure 5 shows that the order with respect to water is first in the neighborhood of the dotted line of Figure 6. On the other hand, at zero DMF concentration (extreme right of Figure 6) the solvent is composed of water and piperidine only, in which medium the order has

TABLE VIII

Effect of Varying the Piperidine and DMF Concentrations.

DMF Run No.	Piperidine Conc.	DMF Conc.	Rate Constant x 10^4
14	2.03	9.10	6.45
15	3.38	7.28	9.09
16	4.06	6.37	9.59
17	4.78	5.46	9.69
18	5.41	4.33	9.30
19	5.41	4.33	8.99
20	6.09	3.64	9.32
21	6.76	2.73	8.71
22	7.44	1.82	7.53
23	8.12	.91	6.51

The water was fixed at 7.41 molar and the piperidine and DMF were varied to maintain a constant volume.

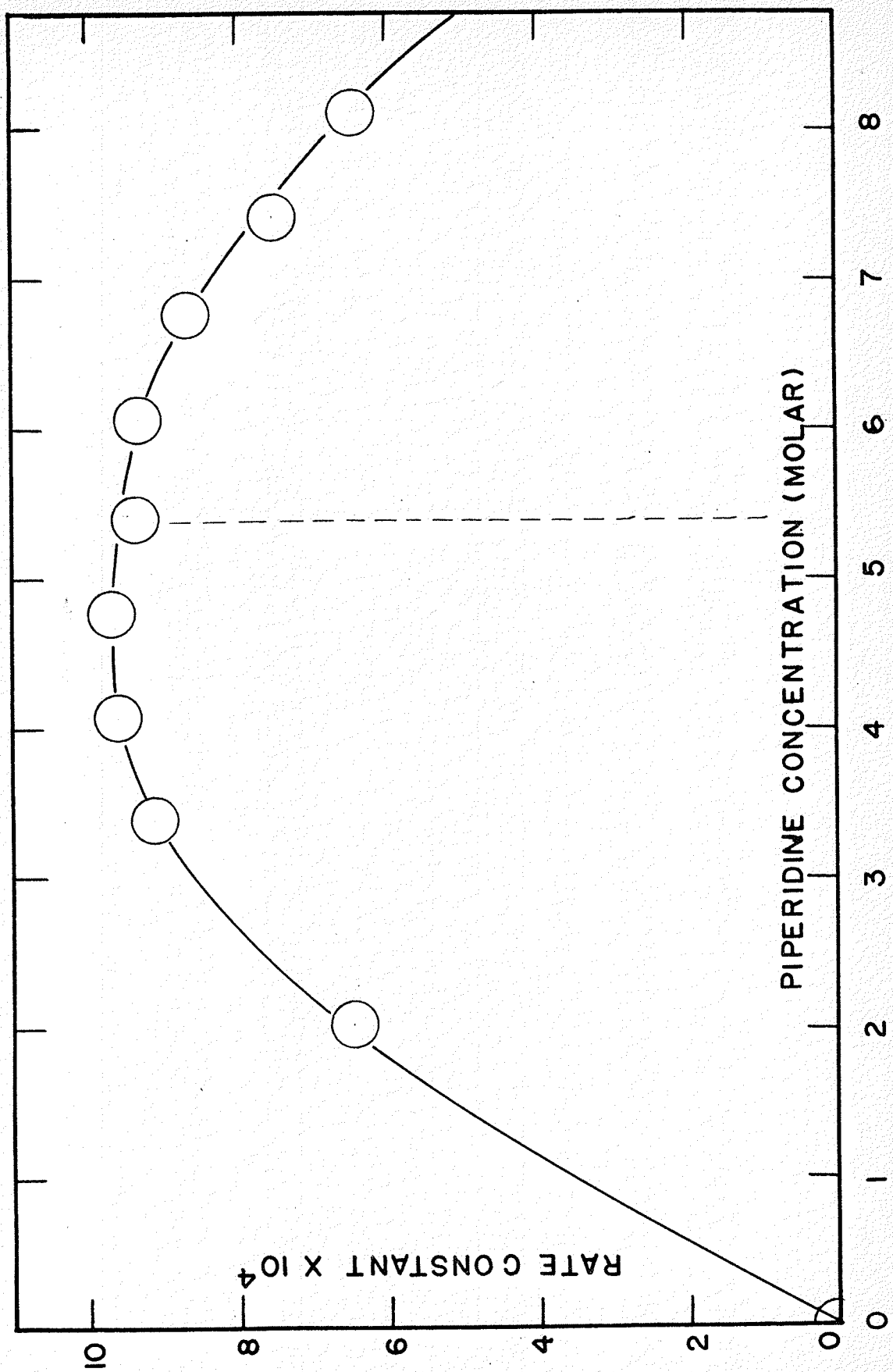


Fig. 6. Relationship between the rate constants and the piperidine concentration at a fixed water concentration of 7.41 molar.

previously been shown to be one-half with respect to water and three-halves with respect to piperidine. That these orders apply at zero DMF concentration in Figure 6 is confirmed by the fact that the extrapolated point at the right hand margin of Figure 6 falls on the $[PH]^{3/2}[H_2O]^{1/2}$ line of Figure 4. It is evident, then, that the order with respect to water increases, and consequently the mechanism of the reaction changes, with increasing DMF concentration. It is, therefore, not surprising that the data of Figure 6 cannot be fitted to any reasonable linear plot.

The change in mechanism could take place by two methods. (1) There may be one mechanism in which the structure of the transition state varies continuously as the medium changes from non-polar to polar. Or, (2) there may be two mechanisms competing with each other, one of which is more favored by the polar medium than the other. If we let this order be n with respect to piperidine in the new medium, then the rate expression for the reaction would be

$$-\frac{d[SH]}{dt} = x[SH][H_2O]^{1/2}[PH]^{3/2} + y[SH][H_2O][PH]^{n}.$$

At zero DMF concentrations (right hand margin of Figure 6) the y term is negligible and the reaction obeys the old kinetics. Increasing DMF concentration apparently favors the y term so that at moderate DMF concentrations both x and y terms participate. At a sufficiently high DMF concentration (dotted line in Figure 6) the x term becomes

negligible and the reaction obeys the new kinetics. Of course, the new mechanism could only displace the old if the new mechanism produces a greater rate of reaction than the old at the same reagent concentrations. Figure 6 shows that the rate by the new mechanism (dotted line) exceeds that by the old (right margin) even when the reagent (piperidine) concentration is greater for the old mechanism than the new.

When the piperidine concentration is kept constant and the water and DMF concentrations varied (DMF increases as water decreases) a similar mechanism change is observed.

TABLE IX

Effect of Varying the DMF Concentration

Piperidine Concentration fixed at 6.09 molar.

DMF Run No.	Water conc.	DMF conc.	Rate Constant x 10^4
28	3.71	4.31	4.96
29	7.41	3.64	9.21
30	11.10	2.73	11.70
31	14.82	1.82	12.75

The data of Table IX plotted in Figure 7 show this. It is seen that at low water (high DMF) concentrations the order with respect to water is unity, but as the water concentrations increase (DMF decreases) the order with respect to water falls off.

The observed increase in the order with respect to water from one-half to unity as the reaction medium is changed from piperidine or a piperidine-toluene mixture to a piperidine-DMF mixture suggests that the hydroxylic reagent changes from hydroxide ion in the old mechanism to water molecule in the new. Since hydroxide ion is the nucleophilic reagent in the old mechanism it is reasonable to suppose (although it is not proved) that water is the nucleophilic reagent in the new one.

This implies that in a piperidine-toluene medium the reaction chooses the most nucleophilic reagent available (hydroxide ion) even though it is present in much lower concentration than the weaker nucleophiles piperidine and water; while in a piperidine-DMF medium the reaction can use the weaker but more plentiful nucleophile, water. That this hypothesis is not unreasonable can be seen from a consideration of the Leveling Effect (15). In a water solution, perchloric and hydrochloric are strong acids and very nearly completely ionized, whereas in a less polar medium such as ether, perchloric is a much stronger acid than hydrochloric. Increasing the polarity of solvent decreases the spread in acid strength between the two acids. Hence it seems not unlikely that increasing the polarity of solvent

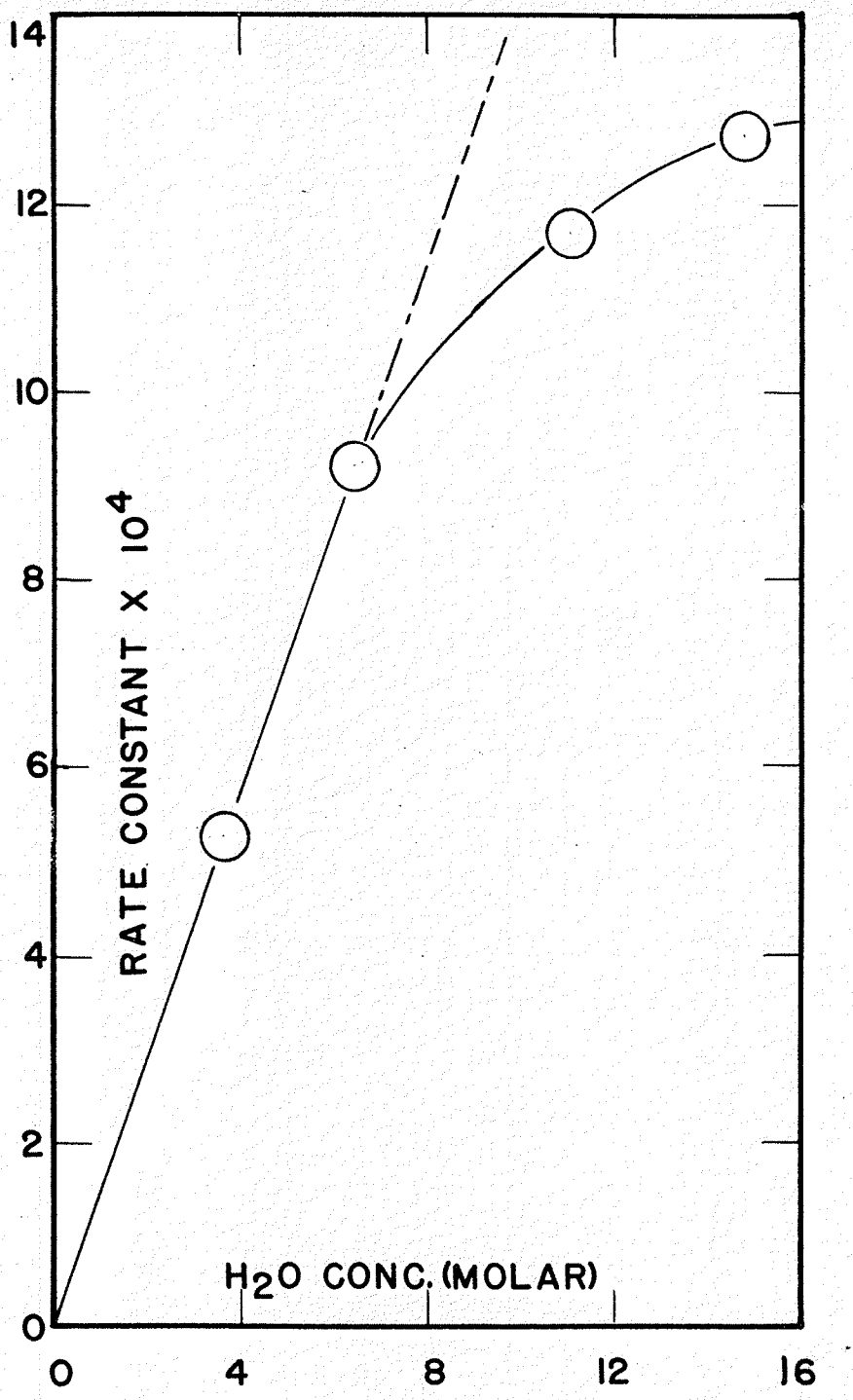


Fig. 7. Relationship between the rate constants and the water concentration with the DMF concentration decreasing with increasing water concentration.

should decrease the spread in nucleophilicity among the hydroxide ion, water and piperidine. DMF is one of the most polar solvents known (dielectric constant ϵ = 118 compared to ϵ = 78 for water) so that replacing piperidine (ϵ = 5.9) in Figure 6 or toluene (ϵ = 2.3) in Figure 5 by DMF might well reduce the difference in nucleophilicity between hydroxide ion and water to such an extent that the concentrational advantage of water would make it the effective nucleophile. Some support for this theory is found in the fact that the deviation from simple orders is greater when DMF replaces the non-polar piperidine (Figure 6) than the polar water (Figure 7).

If the above interpretation of the data from reaction mixtures containing DMF is correct, it should be instructive to study the effect of varying the DMF concentration at fixed concentration of water and piperidine. It might be expected that at low DMF concentrations the old mechanism would apply and added DMF should have only a small accelerating (solvent) effect on the rate; the plot of the rate vs. DMF concentration should have a small positive slope. As the DMF concentration increased, the new mechanism should begin to participate and the slope of the plot should increase. At some sufficiently high DMF concentration the contribution of the old mechanism should become negligible and further addition of DMF should have only a solvent effect again; the slope of the plot should decrease.

TABLE X

Effect of Varying the DMF Concentration.

Water concentration fixed at 7.41 molar

Piperidine concentration fixed at 5.26 molar.

DMF Run No.	DMF Conc.	Toluene Conc.	Rate Constant x 10^4
24	0	3.12	1.83
25	1.82	1.86	3.91
26	3.64	.62	7.65
27	4.33	0	9.30

The data of Table X plotted in Figure 8, show the results of an attempt to observe these predicted changes by measuring the rate in a series of solutions in which the water and piperidine concentrations were fixed while the DMF concentration was varied by replacing various amounts of it with toluene. It can be seen that the small positive slope at low DMF concentrations is observed, and that the slope increases at higher DMF concentrations but the slope does not fall off at still higher DMF concentrations as predicted.

Three interpretations of the failure to observe a decrease in the slope in Figure 8 are possible. (1) Perhaps the DMF concentration never became great enough to make the contribution of the old mechanism negligible. (2) Perhaps DMF exerts a strong

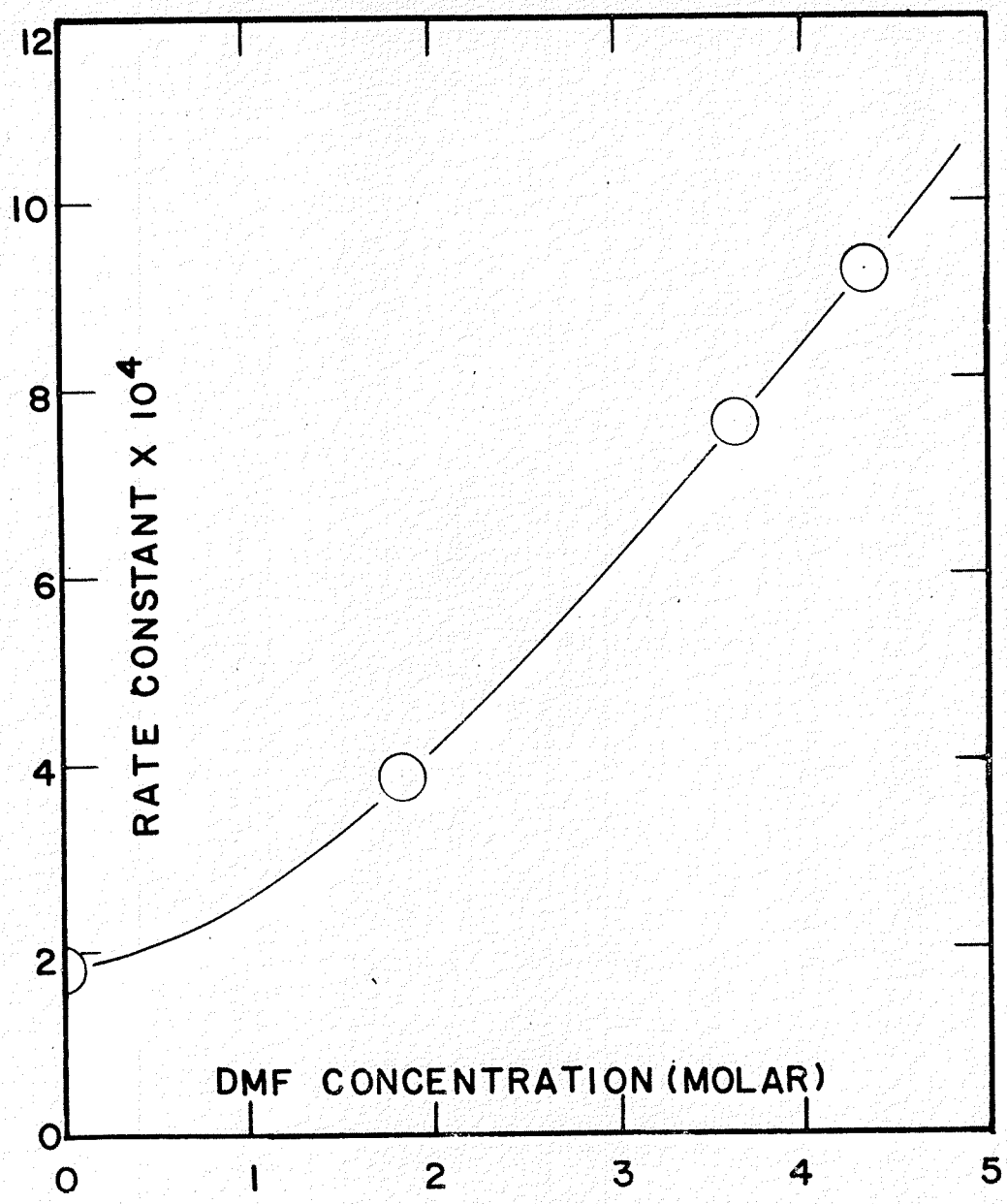


Fig. 8. Relationship between the rate constants and DMF concentration at fixed water and piperidine concentrations.

solvent effect on the new mechanism. (3) Perhaps DMF participates in the new mechanism as a reactant. The third possibility seems very unlikely since DMF should be very poor as either a nucleophile or a proton donor. Furthermore, when either water or piperidine is left out of the reaction mixture the rate is negligible, so that it seems very probable that water and piperidine are still the effective reactants. Nor is it easy to see why the new mechanism should have a much larger solvent effect than the old as proposed in the second possibility, since reactants and products are the same in both cases. The first of the three possibilities is not very attractive either, since Run 27, Table X, of Figure 8 is almost identical with Run 19, Table VIII, of Figure 6 and Run 3, Table VII, of Figure 5. Since the new mechanism is supposed to be in control in the last two of these runs the same should apply to the first. Of course, there is no assurance that the change in mechanism has reached its limit in the range of solvent concentrations used in Figure 5 and 6. The supposition that it has rests on the observation that the order with respect to water has changed from one-half to one. It is conceivable that at even higher DMF concentrations further mechanism changes might occur. Examination of the order with respect to water and piperidine at even higher DMF concentrations might answer these questions, but this was not attempted in the present investigation.

EXPERIMENTAL METHOD

EXPERIMENTAL METHOD

Materials.

(1) Purification of Materials.

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 and stored over KOH pellets. Spectrophotometric analysis of a sample from this fraction detected the presence of water to the extent of .023 molar.

Toluene. Toluene was used as one of the solvents for the silane in the hydrolyses. 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 the fifteen-plate column. The fraction boiling at 110.5° C. (740 mm.) was collected and stored over sodium wire.

Dimethylformamide. Dimethylformamide employed as a solvent in the hydrolyses was purified according to the method of Rochow and Gingold (48). Benzene (50 ml.) was added to 500 ml. of dimethylformamide and distilled through the fifteen-plate column. The benzene-water azeotrope and the excess benzene were distilled and the fraction boiling in the range 151-2° C. (740 mm.) was

collected.

Acetone. Employed as one of the solvents, acetone was purified by the method of Vogel (55). Acetone (400 ml.) was refluxed with sodium iodide (100 gm.) for 30 minutes. The solution was then cooled to -10° C. and the sodium iodide-acetone complex crystallized out as large needles. The crystals were placed in a distilling flask and on being heated the purified acetone distilled over at 56.1° C. (740 mm.).

Nitrobenzene. Nitrobenzene was purified by the addition of benzene and distillation through the fifteen plate column. The benzene-water azeotrope and the excess benzene were distilled and the fraction boiling in the range of 209-10° C. (740 mm.) was collected.

Dioxane. Employed as solvent in the silane hydrolyses as well as in spectrophotometric analyses, the dioxane was purified according to the method of Fieser (14). Dioxane (1000 ml.) concentrated hydrochloric acid (14 ml.) and water (100 ml.) were refluxed for 12 hours during which time nitrogen gas was bubbled through the solution to entrain the acetaldehyde, produced in the decomposition of dioxane. On cooling, the solution was treated with potassium hydroxide pellets until they no longer dissolved. The dioxane was decanted into a clean flask and refluxed with sodium for 12 hours. The solvent was then distilled from the sodium and the fraction boiling in the range 100.5-101° C. (740 mm.) was collected.

Water. The water was purified by an alkaline permanganate distillation followed by three other distillations from an all Pyrex glass still.

(2) Preparation of Materials.

Triphenylsilane. The triphenylsilane was prepared by the reduction of the corresponding chlorosilane using lithium aluminum hydride as reducing agent (18). The reduction proceeded according to the following equation.

$$4\ (C_6H_5)_3\ SiCl + LiAlH_4 \longrightarrow 4\ (C_6H_5)_3\ SiH + LiCl + AlCl_3.$$

Triphenyl chlorosilane, 4.4 gm. (.015 mole) and lithium aluminum hydride, 0.57 gm. (.015 mole) were placed in 150 ml. of anhydrous 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 reduced pressure (1 mm.). The fraction boiling in the range 121-23° C. was collected, which solidified on cooling to room temperature.

Recrystallization from petroleum ether (boiling range 30-60° C.) yielded 2.6 gms. of triphenylsilane (m.p. 44° C. uncorrected).

During the course of this investigation twelve such reductions were carried out. The yields of these preparations ranged from 66 to 75% of the theoretical yield.

N-Alkyl Piperidines.

The employment of N-alkyl piperidines was originally intended to determine the effect of base strength on the rate of hydrolysis. The base strengths of these various amines are included in the table containing the results of this series of kinetic runs. Quinuclidine although a special type of N-alkyl piperidine will also be included under this section of preparation of materials.

The N-alkyl piperidines have been prepared by several methods, but in rather poor yields. Several groups of workers (8, 27, 30, 37) have prepared N-alkyl piperidines by the direct action of alkyl iodides on piperidine using a variety of conditions to attain the reaction. The yields in these preparations ranged from 25 to 40% of the theoretical yield. The first of these preparations was carried out by Ladenburg (37) who prepared alkyl piperidines by gently heating the alkyl halide and piperidine. In all these direct syntheses the low yields of the alkyl-piperidines can be attributed to the formation of quaternary salts. Attempted decomposition of these salts caused the rupture of the piperidine ring. Braun (4) succeeded in preparing a series of N-alkyl piperidines using 1,5-dibromopentane and primary alkyl amines. The yields in this investigation were somewhat higher, ranging up to 60%.

Japanese investigators (49) prepared N-ethyl piperidine employing glutaramide as the starting material which they treated with potassium metal to form the potassium salt. This product was

then reacted with ethyl iodide, which after reduction of the two carbonyl groups yielded N-ethyl piperidine. The yields in this synthesis were not reported but from the length of this synthesis, they would not be expected to be high. Another group of Japanese investigators (41) has prepared N-ethyl piperidine in excellent yield by reacting piperidine with ethanol at 30 atmospheres pressure and 225-230° temperature. The yields were over 90%.

N-ethyl piperidine. In this investigation N-ethyl piperidine was prepared by Ladenburg's method and by two new methods. The first method consisted of preparing an aqueous solution of piperidine (.25 mole) in 100 ml. of water contained in a 300 ml. flask fitted with reflux condenser and dropping funnel. The employment of an aqueous solution of piperidine was intended,to reduce by dilution, the vigor of the reaction and so reduce the formation of quaternary salts. Ethyl iodide (.25 mole) was added dropwise, with stirring, at a rate so that the temperature did not exceed room temperature. After all the alkyl halide had been added the flask was slowly warmed to 65° C. when the solution separated into two layers. The oily layer was taken up in ether and the ether extract dried with solid potassium hydroxide. Distillation of the dried extract yielded 10.6 gm. of N-ethyl piperidine boiling in the range 127-129° C. The percent yield was 38% .

The action of ethyl iodide on piperidine in the absence of a solvent even at 0° C. produced a large amount of the quaternary

salt. The dilution effect due to added water did reduce the amount of the quaternary salt formed, however, even in this case, over 50% of the alkyl halide was involved in the salt formation resulting in low yields of the alkyl piperidine. If one of the groups of the quaternary salt were hydrogen it was thought that ethyl iodide might add resulting in the formation of the hydrochloride of N-ethyl piperidine. The decomposition of this salt would yield the desired alkyl piperidine.

Piperidine hydrochloride was chosen for this second attempt to prepare N-ethyl piperidine. Piperidine hydrochloride, 60 gm. (.5 moles) was dissolved in 150 ml. of water contained in a 300 ml. flask fitted with a reflux condenser. Ethyl iodide, 78 gms. (.5 moles) was added to the aqueous solution and the flask immersed in an ice bath. The insoluble ethyl iodide formed a lower layer in the flask. Potassium hydroxide pellets 70 gms. (1.3 moles) were added slowly, with occasional stirrings. The reaction was found to be occurring essentially at the interface of the aqueous and alkyl halide layers. The reaction with a potassium hydroxide pellet at the interface was vigorous with the formation of small droplets of oil which rose to the surface of the aqueous layer. These droplets were the N-ethyl piperidine which is lower in density than water. The reaction solutions were occasionally stirred to prevent the accumulation of potassium hydroxide pellets in the alkyl halide layer. With the final addition of the pellets the denser and lower layer of

alkyl halide had disappeared forming in its stead a new lighter oily liquid layered over the aqueous solution.

The oily layer was taken up in ether and the ether extract dried over solid potassium hydroxide. Distillation of the dried ether extract yielded 45.2 gms. of N-ethyl piperidine boiling in the range 127-129°C, $n_D^{25} = 1.4443$. A second preparation using the same quantities of starting materials yielded 49.3 gms of N-ethyl piperidine (88%).

Spectrophotometric analysis of the N-ethyl piperidine detected the presence of 5% of piperidine. This was duly removed by the addition of acetyl chloride followed by a redistillation.

N-alkyl piperidines. The excellent yields obtained in the preparation of N-ethyl-piperidine by this new method prompted further investigation. Piperidine hydrochloride was reacted with a variety of alkyl halides to determine what the limitations were with respect to the alkyl halide. The results of this series of preparations are outlined in Table XI. The action of bromobenzene on piperidine hydrochloride was tested and it was found that no reaction took place. After the addition of alkali had been completed, the oily liquid obtained was distilled and found to contain only piperidine and bromobenzene.

The reaction was also tested to determine whether this was a general method of preparing tertiary amines from secondary amines.

TABLE XI

Preparation of N-Alkyl Piperidines

Piperidine Hydrochloride	Alkyl Halide[a]	Product	Boiling Point[b]	Index of Refraction (25°C.)	Weight (gms)	Yield (%)
.115 mole	Ethyl Bromide	N-ethyl Piperidine	127-29° (130.5)	1.4443 (1.4440)	9.8	75
.115	Propyl Bromide	N-propyl Piperidine	146-48° (152)	1.4453 (1.4446)	9.6	66
.115	Isopropyl Bromide	N-Isopropyl Piperidine	147-48° (151)		8.7	60
.115	Ter.-butyl Chloride	Ter.-butyl Alcohol				
.115	Ter.-butyl Bromide	Ter.-butyl Alcohol				
.115	N-amyl Bromide	N-n-amyl Piperidine	193-95° (198)	1.4513 (1.4498)	14.4	88
.25	Ethylene Chlorohydrin	β-N-piperidyl Ethanol	171-72° (172)		24.1	74
.25	Ethylene Dibromide	β-N-piperidyl Ethanol[c]	171-72° (172)		8.8	27

[a] The mole quantity of alkyl halide was equal to the corresponding molar quantity of piperidine hydrochloride employed.

[b] The recorded boiling point is at 740 mm. and is uncorrected. The values in parenthesis are the corresponding literature values.

[c] The reaction of ethylene dibromide did not yield the expected products β-N-piperidyl ethyl bromide and 1,2-N-piperidyl ethane but β-N-piperidyl ethanol and the potassium salt of an alcohol. The potassium salt when dissolved in water yielded an oil boiling at 171-72° which was proved to be β-N-piperidyl ethanol by heating the product obtained from the ethylene chlorohydrin reaction with 50% KOH solution which yielded a precipitate of the potassium salt on cooling.

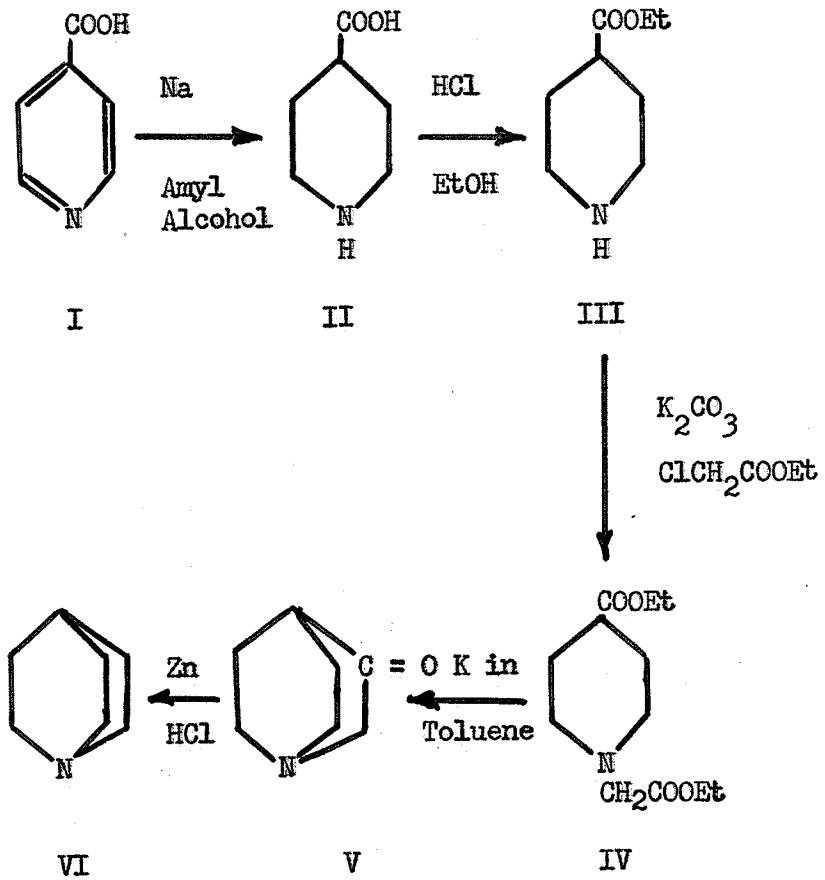
The hydrochlorides of three secondary amines, dimethylamine, diethylamine and diphenylamine were each treated with ethyl iodide and bromobenzene. The results in all cases were negative; the free amine and bromobenzene were the products obtained in the bromobenzene series of reactions, whereas in the other series the free amine and small quantities of ethyl iodide were isolated.

The results of this investigation together with the results of Table XI indicate that the reaction in its present form is restricted to piperidine and primary or secondary alkyl halides. The isolation of t.-butyl alcohol from the reactions involving the corresponding bromide and chloride is not too surprising in view of the fact that tertiary halides are readily hydrolyzed. The addition of potassium hydroxide pellets to the aqueous solution would present a suitable hydrolyzing solution.

Quinuclidine. Quinuclidine was first prepared by Loffler and Steitzel (40) employing a series of reactions previously used by Koenigs and Bernhardt (35, 36) for the preparation of 2-ethyl quinuclidine. Picoline was condensed with formaldehyde and the resulting β-4 pyridyl ethanol was reduced with sodium and alcohol; treatment of the product with hydrogen iodide gave β-4 piperidyl ethyl iodide which underwent an intramolecular rearrangement to quinuclidine hydrochloride. The free base was reported as a viscous liquid boiling at 141°C.

Meisenhiemer (42) repeated this synthesis. He increased the yield of the rearrangement from 10% to 70% and described the base as a volatile solid with a melting point of 158° C. The drawback in this synthesis was the first step involving the condensation of γ -picoline with formaldehyde to give a 1% yield of the β -4 pyridyl ethanol. Brown and Sujishi (6) eliminated this difficulty by employing the then commercially available β -4 pyridyl ethanol.

Originally it had been intended to prepare quinuclidine by the method of Brown and Sujishi, however, the β -4 pyridyl ethanol was no longer available commercially and an alternative synthesis was chosen. This synthesis, reported by Clemo and Metcalfe (9) can be outlined as follows:-



Ethyl Piperidine-4-carboxylate (III). Isonicotinic acid, (I), 20 gm. (.16 mole) was dissolved in hot amyl alcohol (1200 ml.) and treated with 90 gm. (3.9 mole) of sodium metal. The clear solution was cooled and poured into 2 litres of water, the amyl alcohol was separated, then washed with dilute HCl followed by water. The hydrochloric acid and water washings were added to the aqueous layer, which was then acidified with concentrated hydrochloric acid and evaporated to dryness. The residue was extracted five times with 200 ml. portions of ethyl alcohol (95%) and the extract evaporated to dryness. 250 ml. of absolute ethyl alcohol saturated with hydrogen chloride gas were added to the residue, allowed to stand 12 hours and refluxed for 5 hours more. The ethyl alcohol was distilled until the volume was reduced to 50 ml. and the residue evaporated to dryness. The residue was basified with potassium carbonate and extracted with ether. The ether extract was dried over anhydrous sodium sulphate. Five such ether extracts were combined, the ether distilled and the oily residue fractionated under reduced pressure to give 74.1 gm. of liquid having a boiling point of 74° at 1 mm. and an index of refraction 1.4596 at 25° C. The yield obtained in this step was 59% and comparable to that reported by Clemo and Metcalfe (64%).

Ethyl piperidine-1-acetate-4-carboxylate, (IV). Ethyl piperidine-4-carboxylate, (III), 35 gm. (.22 mole) ethyl chloroacetate, 30 gm. (.24 mole) and anhydrous potassium carbonate, 30 gm. (.22 mole) were

mixed and heated at 110-115°C. for 4 hours. Water was added and the oil taken up in ether. A second portion of ethyl piperidine-4-carboxylate, 39 gm. (.25 mole) was similarly treated, the ether extracts combined and fractionated to give ethyl piperidine-1-acetate-4-carboxylate (41.4 gm.) boiling point 136-138°C. at 1 mm. The yield in this step was 34% and approximately 50% of that reported by Clemo and Metcalfe (64%).

2-Ketoquinuclidine, (V). The above diester, (IV), 41.4 gm. (.17 mole) in toluene (50 ml.) was added to a warm suspension of finely powdered potassium metal, 13 gm. (.33 mole) in toluene (50 ml.) and the mixture heated at 120° for 10 minutes; it then solidified and was again heated at 110° for 3 hours. After cooling, absolute alcohol was added to destroy the excess potassium, this was followed by water (20 ml.) and concentrated hydrochloric acid (250 ml.). The solution was heated in a water bath for 14 hours. After evaporation to dryness, the residue was basified with potassium hydroxide solution (50%) and the product extracted with ether. The pale yellow extract, dried over anhydrous potassium carbonate was added to a warm alcoholic solution of picric acid. The keto picrate which precipitated after crystallization from alcohol, was decomposed with a slight excess of KOH solution. The product, extracted and dried (solid KOH) in ether gave on distillation the ketone (6 gm.

boiling point 120° at 14 mm.) as a crystalline solid. Recrystallization from petroleum ether (boiling range 30-60°C.) gave dendrites melting at 136-137°C. The yield was 28% in this stage.

Quinuclidine (VI). Ketoquinuclidine, (V), 5 gm. (.04 mole) was refluxed with amalgamated zinc (90 gm.) and concentrated hydrochloric acid (250 ml.). More acid (100 ml.) was added and refluxed for 24 hours. The acid solution was decanted and basified then steam distilled. The distillate was acidified with hydrochloric acid and evaporated to dryness. The yield of crude quinuclidine hydrochloride was 1.4 gms. The yield in this final stage of the synthesis could not be compared to the work of Clemo and Metcalfe who did not report the yields obtained in the last two steps of their synthesis.

The poor yields of the intermediate steps produced a much smaller yield of the final product which would be too small for a kinetic run and so this project was abandoned.

Kinetic Runs.

The hydrolysis of triphenylsilane employing a piperidine-water solution may be represented by the following equation

$$OH^- + (C_6H_5)_3SiH + PH \longrightarrow (C_6H_5)_3SiOH + H_2 + P^-$$

where PH represents piperidine. Since one of the products of the reaction is hydrogen gas, the reaction lends itself to a manometric study.

Apparatus. The kinetic runs were carried out in the apparatus shown in Figure 9. The reaction flasks were 25 ml. distilling flasks (A) with the side arms removed. The reaction flask was connected to an open manometer (M) by means of Tygon tubing. Both the reaction flask and the manometer were clamped to a long brass rod (R) but the reaction flask had to be held with a movable clamp since previous investigators (11, 45) have shown that to insure a smooth evolution of hydrogen the reaction flask had to be agitated during the reaction. Consisting of an open manometer and reaction flask attached to a brass rod, the reaction apparatus required for a kinetic run was, therefore, a single unit which could be easily manipulated for both loading and cleaning.

Agitation of the reaction flask was provided by a stirring motor (B) to which was connected a cam (C) by a long shaft. The shaft was steadied by the bearing (D). The agitation apparatus was permanently mounted in a glass fronted thermostat maintained at

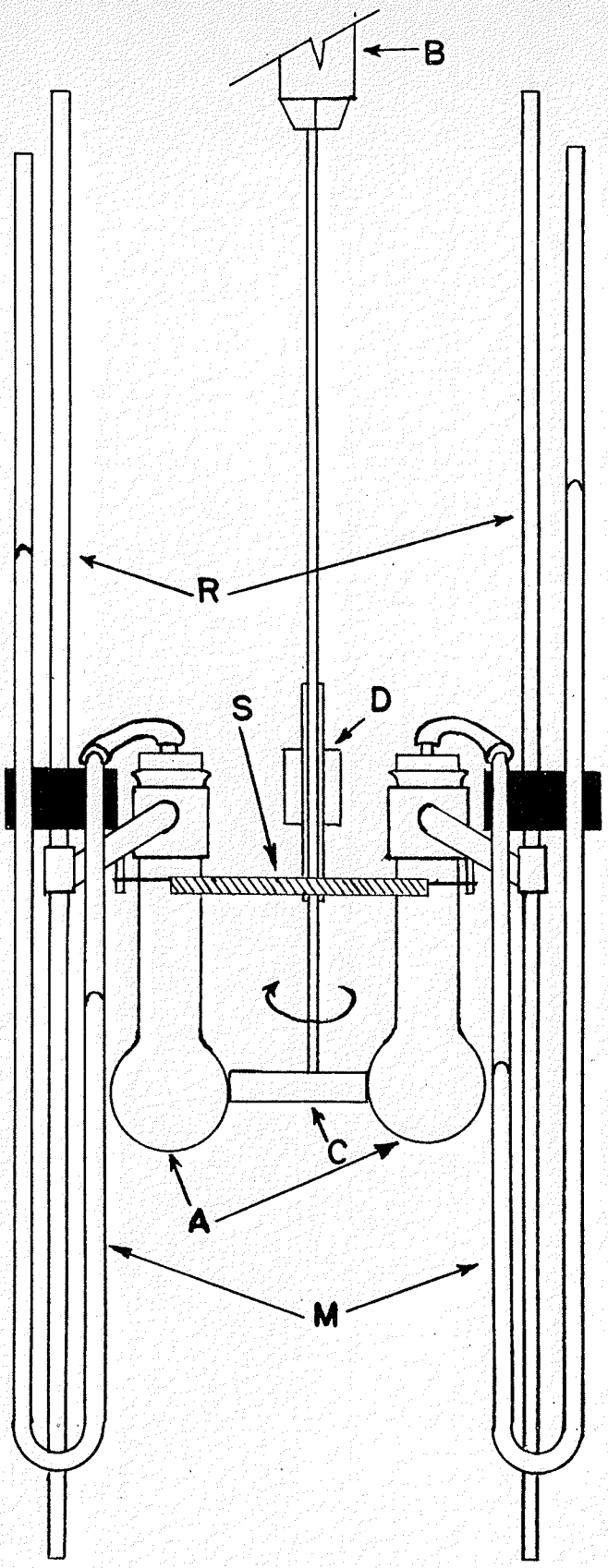


Fig. 9. Apparatus for kinetic runs.

25.00 $\pm$ .01° C.

The reactions were carried out in pairs, thus a reaction unit after being loaded was mounted on either side of the cam (C). The flasks were kept in contact with the cam by means of the spring (S).

Procedure. The kinetic runs were carried out by the following procedure. The water, piperidine and solvent were added directly in the reaction flask. The proportions of these components were varied to maintain the fixed volume of 15 ml. of solution. The water concentration in the lower regions (up to 3 molar) was determined by titration with Karl Fischer Reagent. In the region of higher water concentrations the water was weighed. The upper limit of solubility of toluene was determined by adding Methylene Blue to a sample of piperidine-water solution and examining this solution under a microscope. Samples from a solution 16 molar in water showed that two phases were present. The water concentrations were calculated on the assumption that there was no change in the volume upon mixing of the reactants. The silane was weighed out separately and introduced when all was in readiness for a run. The silane sample used in the runs was .2000 gm. which in conjunction with the fixed volume of 15 ml. of solution produced sufficient gas to give a final manometer reading of 34.00 cm.

The silane sample was introduced into the reaction flask containing the reaction solution, the system stoppered and the

stopwatch started. The apparatus was then immersed into the thermostat and clamped rigidly against the cam. The spring was connected and the stirring motor started.

The progress of the reaction was followed by reading the increase of pressure with time by means of a vertical reading cathetometer. The rate of reaction was calculated by the method of least squares (10) from log $(P_{\infty} - P)$ and the time interval t. In the logarithm expression P_{∞} is the manometer reading that the hydrogen gas exerted at the completion of the reaction and P is the manometer reading of the gas at time t. The hydrolyses were carried out under conditions yielding pseudo-first order kinetics, that is, all the reagents except silane were in excess. A good linear plot was obtained to 85% completion when toluene was employed as solvent and to 97% when DMF was used. The data and plot of a typical run carried out in toluene are presented in Table XII and Figure 10, and the data and plot of a typical run carried out in DMF are shown in Table XIII and Figure 11.

In determining the root mean square deviation of the points from a given run, the error was extremely small (see Figures 10 and 11), being about .1% in magnitude. It was felt a truer picture of the error could be obtained from the reproducibility of the rates obtained from the check runs which are tabulated below in Table XIV. The error in the rate constant was taken as the largest deviation from the mean value and was found to be $\pm$ .03 x 10^{-4} for runs in toluene solvent.

TABLE XII

Check Run 7.

Hydrolysis of Triphenylsilane in Piperidine Containing 1.86 Moles of Water per Liter at 25°.

Weight of Sample = 0.2000 gm.; Thermostat temperature = 25°; Pressure = 741 mm.; 10 ml. of piperidine-water solution (1.86 molar) 5 ml. of toluene (3.11 molar).

Time Min.	Manometer Reading		Pressure Difference (cm.)	P_∞-P	log P_∞-P
3	21.61	26.26	4.65	29.35	1.4675
10	20.93	26.98	6.05	27.95	1.4464
15	20.38	27.43	7.05	26.95	1.4306
20	19.92	27.92	8.00	26.00	1.4150
30	19.03	28.80	9.77	24.23	1.3843
40	18.17	29.66	11.47	22.53	1.3528
50	17.42	30.36	12.94	21.06	1.3234
60	16.73	31.09	14.36	19.64	1.2932
70	16.03	31.72	15.69	18.31	1.2627
80	15.44	32.32	16.88	17.12	1.2335
90	14.74	32.90	18.16	15.84	1.1998
105	14.06	33.69	19.63	14.37	1.1574
120	13.30	34.29	21.09	12.91	1.1109

P_∞ = 34.00 cm.

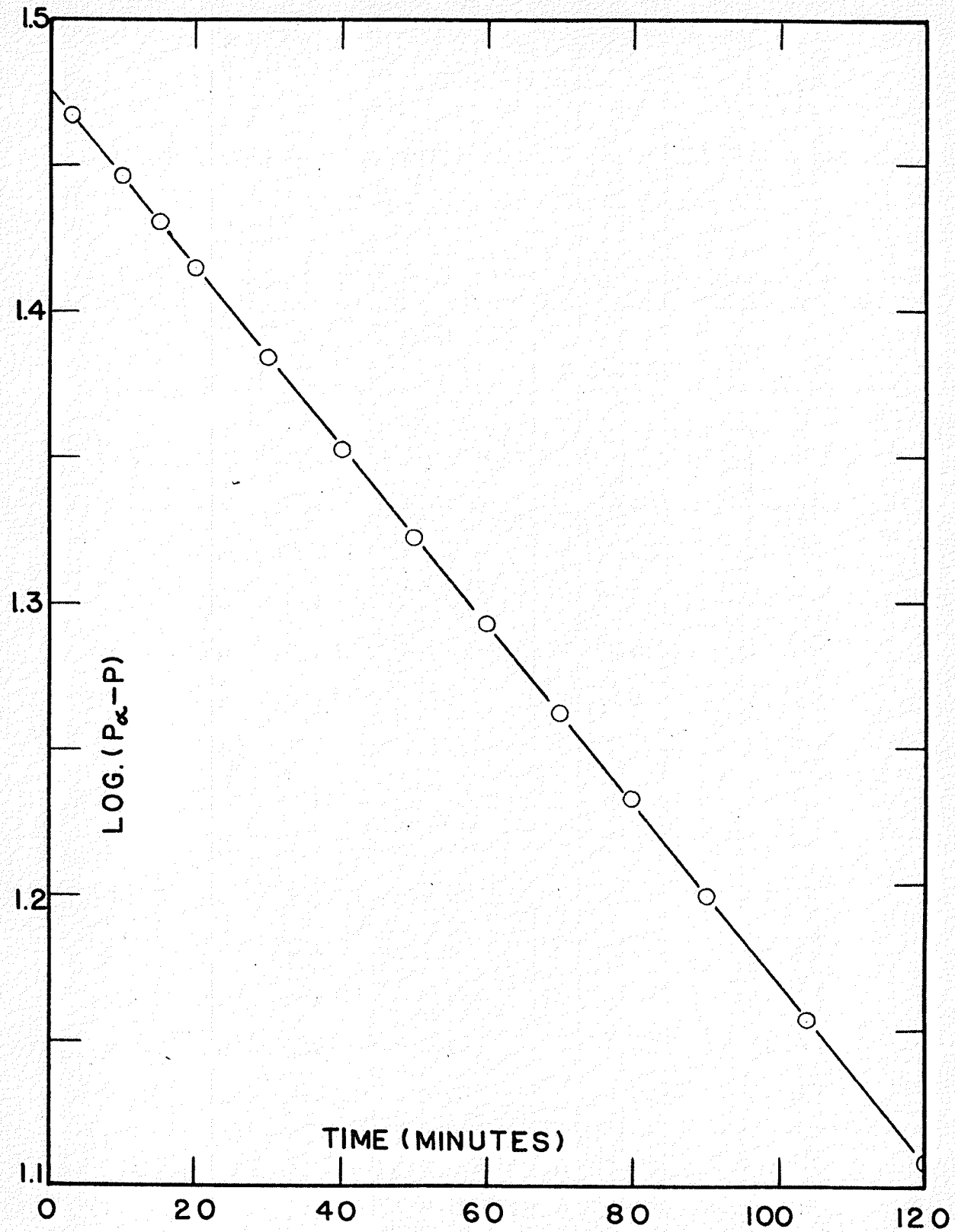


Fig. 10. Hydrolysis of triphenylsilane in toluene.

TABLE XIII

DMF - Run 3

Hydrolysis of Triphenylsilane in Piperidine Containing 7.41 Moles of Water per Liter at 25°.

Weight of Sample = 0.2000 gm.; thermostat temperature = 25° C.
Pressure = 737.4 mm; 8 ml. of Piperidine (5.41 molar)
2 gm. of Water (7.41 molar); 5 ml. of DMF (4.33 molar).

Time Min.	Manometer Reading		Pressure Difference (cm.)	P_∞-P	log P_∞-P
3	21.47	27.50	6.03	27.97	1.4467
10	17.08	31.76	14.68	19.32	1.2860
15	14.55	34.18	19.63	14.37	1.1574
20	12.88	35.86	22.98	11.02	1.0422
25	11.53	37.17	25.64	8.36	.9222
30	10.60	38.10	27.50	6.50	.8129
35	9.77	38.89	29.12	4.88	.6884
39	9.25	39.32	30.07	3.97	.5988
53	8.24	40.42	32.18	1.82	.2601

P_∞ = 34.00 cm.

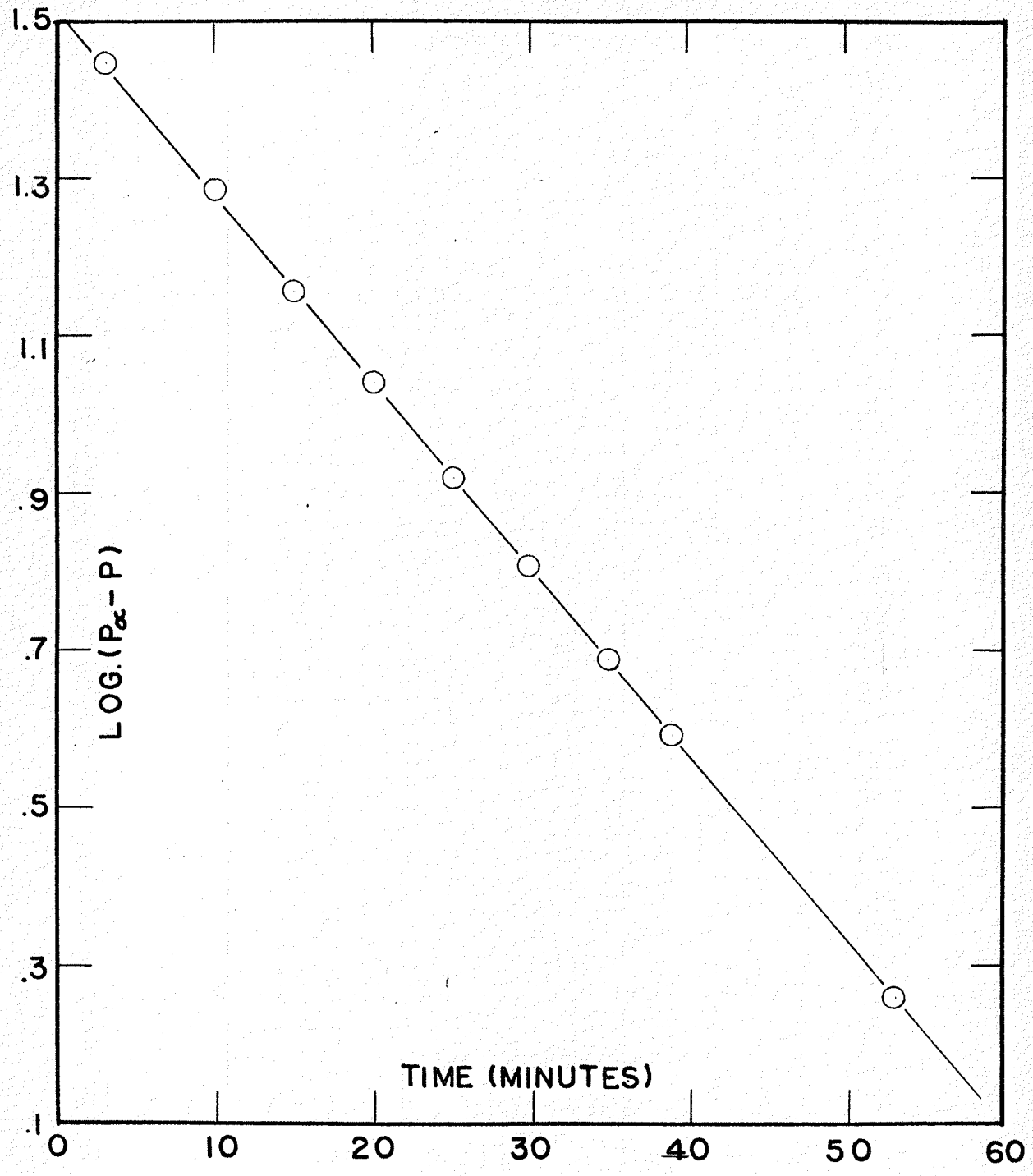


Fig. 11. Hydrolysis of triphenylsilane in DMF.

The error in rate for the kinetic runs carried out in dimethylformamide was obtained from the largest deviation of rate constants at the same concentration of reactants. This was found to be 0.5×10^{-4} and is therefore the error assigned to the rate constants obtained from kinetic runs carried out in dimethylformamide.

TABLE XIV

Hydrolyses of Triphenylsilane at 25°.

Check Run No.	Piperidine (Molar)	Water (Molar)	Toluene (Molar)	Rate Constant x 10^4 sec^{-1}
1	6.42	1.86	3.11	1.22
2	6.42	1.86	3.11	1.22
3	6.42	1.86	3.11	1.19
4	6.42	1.86	3.11	1.18
5	6.42	1.86	3.11	1.21
6	6.42	1.86	3.11	1.20
7	6.42	1.86	3.11	1.17
8	6.42	1.86	3.11	1.21
				Mean 1.20 ± .03.

The rate constants from this series of runs were in good agreement with those obtained in a previous investigation (7), which were obtained from the increase in volume at constant pressure ($k = 1.27 \times 10^{-4}$ sec.$^{-1}$). A comparison of rates could not be made

with the rates obtained by Dunn (11) since the investigation had been carried out at higher temperatures.

Preliminary Experiments. During the early stages of this investigation several samples of triphenylsilane were prepared and kinetic runs showed that the rate constants at fixed concentration of reactants did not agree, although all samples had the same melting point (44°C.). Further, the pressures exerted by the gas at completion of the runs were in good agreement whereas the rate constants varied from 1.22 to 11.20 x 10^{-4} sec.$^{-1}$.

Isolation of the impurities from a triphenylsilane preparation yielded small amounts of triphenylsilanol, hexaphenyldisiloxane, hexaphenyldisilane and p-terphenyl. Kinetic runs were therefore carried out in which relatively large amounts of these impurities were added with no observable change in the rate constant. Samples of silane subjected to ultraviolet and sunlight likewise produced no change in the rate constant.

Newer stocks of triphenylchlorosilane when reduced to triphenylsilane did produce consistent rate constants. Although the cause of these erratic results was not determined it could only be attributed to minute quantities of some impurity which behaved as a positive catalyst. During the remainder of this investigation check runs were carried out on new samples of silane to insure against the use of rate constants obtained from erratic samples.

The Kinetic Solvent Isotope Effect. The kinetic solvent isotope effect was calculated from the results obtained in a series of runs employing a hydrolyzing solution of piperidine and deuterium oxide. The deuterium oxide concentration was varied from 1.83 molar to 9.38 molar. The rate constants for this series of runs were determined in the normal manner.

The hydrolyzing solution, because of the presence of the amine hydrogen in piperidine, would contain not only the deuterium oxide initially introduced but also other deuterated species produced by the exchange equilibrium

$$C_5H_{10}NH + D_2O \overset{K}{\rightleftharpoons} C_5H_{10}ND + HOD. \qquad (a)$$

The presence of HOD in the reaction solution produced a further equilibrium

$$H_2O + D_2O \overset{K'}{\rightleftharpoons} 2\ HOD. \qquad (b)$$

The equilibrium constant for the reaction (b) is known to be 3.80 (34) but that for the reaction (a) was not known. In a previous investigation carried out by Dunn and Brynko (7) the equilibrium constant for the reaction (a) was approximated by considering two other exchange equilibrium reactions for which the constants are

known. These reactions are

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

and

$$D_2HO^{+} + D_2O \rightleftharpoons D_3O^{+} + HOD. \qquad (d)$$

The equilibrium constant for the reaction (c) is 0.72 (34) and 0.76 (51) for (d). Since the difference in the exchange constants for the two reactions (c) and (d) is only 5% even though deuterium is being transferred to an oxygen atom in one case and to a nitrogen atom in the other, it seemed reasonable that when deuterium is being transferred to nitrogen in both cases (a) and (c) the difference should be no greater than 5%. The value K = 0.72 was employed as the exchange constant for the above reaction (a).

In order to calculate the kinetic solvent isotope effect the concentrations of the reactants, both normal and isotopically substituted had to be determined. The concentrations of the reactants piperidine, piperidine-d, deuterium oxide, water, and hydrogen deuterium oxide were determined from the following conditions imposed on the reactants

$$(1) \quad PH + D_2O \overset{K}{\rightleftharpoons} PD + HOD \qquad K = 0.72$$

$$(2) \quad H_2O + D_2O \overset{K'}{\rightleftharpoons} 2\ HOD \qquad K' = 3.80$$

(3) PD + PH = y moles (total moles of piperidine employed).

(4) HOD + D_2O + H_2O = x moles (total moles of deuterium oxide employed).

(5) $2D_2O$ + HOD + PD = 2x moles (total moles of deuterium in the deuterium oxide).

The above five conditions were incorporated into a cubic equation, the solution of which yielded the concentrations of the reactants after attainment of equilibrium conditions. That this equilibrium was a rapid process had been proved in a previous investigation (7). The equilibrium concentrations of the reactants are shown in Table XV.

TABLE XV

Moles of Reactants in 15 ml. of Reaction Solution at Equilibrium.

Run No.	Piperidine	Piperidine-d	H_2O	HOD	D_2O
61	.0695	.0269	.0066	.0136	.0074
62	.0695	.0269	.0066	.0136	.0074
63	.0535	.0378	.0066	.0246	.0241
64	.0448	.0525	.0065	.0397	.0645
65	.0376	.0608	.0058	.0493	.1109

The following kinetic expression for the hydrolysis of triphenylsilane has been proved to apply

$$\frac{d[H_2]}{dt} = k[SH][PH]^{3/2}[H_2O]^{1/2}. \qquad (e)$$

When this expression is employed with an isotopically substituted medium it would have to be expanded to the following form

$$\frac{d[H_2 \neq HD]}{dt} = k_H[SH][PH]^{3/2}[D_2O]^{1/2} \neq k_D[SH][PD]^{3/2}[D_2O]^{1/2}. \qquad (f)$$

where D_2O represents the equilibrium species H_2O, HOD, and D_2O and k_H designates the contribution from the normal reactants and k_D the contribution of the isotopic reactants.

However, this expression must be modified before a calculation of the rate ratio k_D/k_H can be made. Piperidine participates in the reaction in a dual role. Firstly, its participation in the preliminary equilibrium to produce hydroxide ion, gives rise to the terms $[PH]^{1/2}[H_2O]^{1/2}$ in the kinetic expression (e). Both PH and PD can participate in this equilibrium so that in the isotopically substituted medium $[PH]^{1/2}$ in the kinetic expression (e) can be replaced by $[PH \neq PD]^{1/2}$. Wilzbach and Kaplan (32) have pointed out that the autoprotolysis constant of deuterium oxide is about one-fifth that of water which would

indicate that in a deuterium oxide-piperidine medium the deuteroxide ion concentration would be smaller than the hydroxide ion concentration in a piperidine-water medium. However, these investigators have also pointed out that the reactivity of the deuteroxide ion in deuterium oxide is from 20 to 40 percent greater than that of the hydroxide ion in a water medium. That these two opposing factors must compensate each other can be seen in the results of Table XVI which show exceeding good agreement among the rate ratios k_D/k_H in the large range of deuterium oxide concentrations studied.

The solvent isotope effect results from the second role of piperidine in which it acts as proton donor, giving rise to the first power of the piperidine concentration in the kinetic expression (e). In this role piperidine and piperidine-d will react at different rates so that $k\,[PH]$ in the expression (e) must be replaced by $k_H\,[PH] \neq k_D\,[PD]$. Making these substitutions gives rise to the kinetic expression

$$\frac{d\,[H_2 \neq HD]}{dt} = [SH]\,[PH \neq PD]^{1/2}\,[D_2O]^{1/2}\left(k_H\,[PH] \neq k_D\,[PD]\right). \quad (g)$$

Since k_H is known from the reactions in the undeuterated media, the kinetic isotope effect can be calculated by determining the rate ratio k_D/k_H in the kinetic expression (g). The results of the kinetic runs and the isotope effects are shown in Table XVI.

TABLE XVI

Rate Constants for Triphenylsilane Hydrolysis

in Piperidine and Deuterium Oxide.

Run No.	Initial PH Conc. (molar)[a]	Initial D_2O Conc. (molar)[a]	Rate Constant[b] x 10^4	Rate Ratio k_D/k_H
61	6.43	1.83	1.03 (1.22)	.49
62	6.43	1.84	1.04 (1.22)	.50
63	6.09	3.66	1.28 (1.63)	.49
64	5.87	6.66	1.31 (1.80)	.49
65	5.56	9.38	1.42 (2.08)	.49

[a] The equilibrium concentrations can be calculated from Table XV.

[b] The value in parenthesis is the rate of hydrolysis corresponding to the same concentrations of undeuterated reactants.

The results of Table XVI substantiate the rate expression obtained from the kinetic study. If the rate expression was in error then the rate ratio k_D/k_H would hardly be expected to remain constant through the wide range of deuterium oxide concentrations employed.

CONCLUSIONS

CONCLUSIONS

(1) The hydrolysis of triphenylsilane in a non-polar solvent (toluene) has been found to be:

(a) first order with respect to triphenylsilane;

(b) half order with respect to water; and

(c) three halves order with respect to piperidine.

These orders with respect to the reactants indicate that the rate expression for the hydrolysis must be

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

This rate expression which was found to hold through the range of water concentrations from .15 to 14.82 molar, shows that the mechanisms proposed by previous investigators are inconsistent with the kinetics of the reaction.

(2) The following mechanism which is consistent with the above kinetics has been proposed

$$R_3SiH + C_5H_{10}NH \underset{\text{Fast}}{\rightleftharpoons} R_3Si(H)(H)NC_5H_{10}$$

$$OH^- + R_3Si(H)(H)NC_5H_{10} \xrightarrow{\text{Slow}} R_3SiOH + H_2 + C_5H_{10}N^-.$$

The effect of more polar solvent media shows a moderate increase in the rate of hydrolysis at fixed reactant concentrations. The use of a variety of amine bases has shown that the reaction will not proceed with a tertiary amine, indicating that the amine employed in the hydrolysis plays the role of proton donor. These results support the proposed mechanism.

(3) Employing a piperidine-deuterium oxide hydrolyzing solution the kinetic solvent isotope effect (rate ratio k_D/k_H) was calculated to be 0.49. This value, along with the isotope effects determined in a previous investigation and the above mechanism, require that the reaction proceed through a tightly bonded transition state as proposed by Gilman, Dunn and Hammond (17) and amplified by Wilzbach and Kaplan (32).

(4) The hydrolysis of triphenylsilane in dimethylformamide as solvent was found to be first order with respect to water and not half-order as observed in toluene. The change in water order clearly showed that a mechanism change occurred when a more polar solvent was employed. The kinetic order of all the reactants in dimethylformamide was not determined.

(5) A new method for preparing N-alkyl piperidines in good yield has been evolved. This synthesis employs piperidine hydrochloride and a primary or secondary alkyl halide.

BIBLIOGRAPHY

BIBLIOGRAPHY.

1. C. Anfinsen in O. W. Wilson, A.O.C. Nier and S. S. Reimann's "Preparation and Measurement of Isotopic Tracers", Ann Arbor, Michigan, 1946, pp. 61-65.

2. J. Bigeleisen, J. Chem. Phys., 15, 261 (1947).

3. J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

4. V. Braun, Ber., 42, 2052 (1909).

5. G. Briegleb, Z. Electrochem., 53, 350 (1949)

6. H. C. Brown and S. Sujishi, J. Am. Chem. Soc., 70, 2878 (1949).

7. C. Brynko, M. Sc. Thesis, University of Manitoba (1954).

8. A. Cahours, Ann. de Chemie et de Physique 3, 3895 (1905).

9. G. R. Clemo and T. P. Metcalfe, J. Chem. Soc., 1937, 1989.

10. F. Daniels, J. H. Mathews, J. W. Williams and Staff. "Experimental Physical Chemistry", McGraw-Hill Book Co., Inc., New York 1949, pp. 370-371.

11. G. E. Dunn, Ph. D. Thesis, Iowa State College (1951).

12. C. Eaborn, J. Chem. Soc., 1955, 2047.

13. H. Eyring and F. W. Cagle, J. Chem. Phys., 56, 889 (1952).

14. L. F. Fieser's "Experiments in Organic Chemistry", D. C. Heath and Company, New York, 1941, pp. 368-369.

15. J. S. Fritz's "Acid-Base Titrations in Nonaqueous Solvents", The G. Frederick Smith Chemical Co., Colombus, Chio, 1952 pp. 6-7.

16. V. P. Frontas'ev, J. Phys. Chem. (U.S.S.R.) 20, 91 (1946).

17. H. Gilman, G. E. Dunn, and G. S. Hammond, J. Am. Chem. Soc., 73, 4499 (1951).

18. H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 3404 (1951).

19. H. Gilman and G. N. R. Smart, J. Org. Chem., 15, 720 (1950).

20. H. Gilman and R. N. Clark, J. Am. Chem. Soc., 69, 1499 (1947).

21. H. Gilman and S. P. Massie, Jr., J. Am. Chem. Soc., 68, 1128 (1946).

22. H. Gilman, A. G. Brook and L. S. Miller, J. Am. Chem. Soc., 75 4531 (1953).

23. G. Glocker and S. Lind "Electrochemistry of Gases and Other Dielectrics", John Wiley and Sons, Inc., New York, N.Y., 1939, pp. 334-335.

24. W. Gordy, J. Chem. Phys., 7, 93 (1939).

25. N. F. Hall, J. Am. Chem. Soc., 52, 5115 (1930).

26. N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc., 54, 3479 (1932).

27. G. T. Hata, Y. Yokoyama, H. Komatsee and M. Aizawa, Kitasato Arch. Expl. Med., 21, 113 (1948).

28. C. R. Hauser and C. R. Hance, J. Am. Chem. Soc., 73, 5846 (1951).

29. G. Herzberg, "Molecular Spectra and Molecular Structure", Prentice-Hall Inc., New York, 1939 Vol. 1 p. 487.

30. A. W. Hofman, Ber, 14 660 (1881).

31. C. K. Ingold's "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York, 1953 pp. 345-350.

32. L. Kaplan and W. E. Wilzbach, J. Am. Chem. Soc., 77, 1297 (1955).

33. F. S. Kipping and J. E. Sands, J. Chem. Soc., 1921, 849.

34. Kirshenbaum, "Physical Properties and Analysis of Heavy Water", McGraw-Hill Book Co., Inc., New York, 1951.

35. W. Koenigs and K. Bernhardt, Ber., 37, 3244 (1904).

36. W. Koenigs and K. Bernhardt, Ber., 38, 3049 (1905).

37. A. Ladenburg, Ber., 14, 1348 (1881).

38. K. J. Laidler's "Chemical Kinetics", McGraw-Hill Book Co., Inc., New York, 1950, p. 132.

39. W. M. Lauer and W. E. Noland, J. Am. Chem. Soc., 75, 3689 (1953).

40. K. Loffler and F. Steitzel, Ber., 42, 24 (1909).

41. M. Matsumoto, Y. Kishinouye, I. Yamazaki and Y. Nakamura, Coal Tar (Japan), 6, 198 (1954).

42. J. Meisenhiemer, J. Neresheimer and W. Schneider, Ann., 420, 190 (1920).

43. L. Melander, Nature, 163, 599 (1949).

44. W. H. Nebergall and O. H. Johnston, J. Am. Chem. Soc., 71, 4022 (1949).

45. F. P. Price, J. Am. Chem. Soc., 69, 2600 (1947).

46. N. Pushin, Bull. soc. chim, (Belgrade) 15, 9 (1950).

47. Piper and E. G. Rochow, J. Am. Chem. Soc., 76, 4318 (1954).

48. E. G. Rochow and K. Gingold, J. Am. Chem. Soc., 76, 4852 (1954).

49. B. Sakurai, Bull. Chem. Soc. (Japan), 13, 482 (1938).

50. V. J. Shiner, Jr., J. Am. Chem. Soc., 74, 5285 (1952).

51. Suess and Jensen, Naturwissenschaften, 32, 372, (1944).

52. S. Sujishi and Witz, J. Am. Chem. Soc., 76, 4631 (1954).

53. C. G. Swain, R. M. Esteve, and R. A. Jones, J. Am. Chem. Soc. 71, 965 (1949).

54. L. J. Tyler, L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc., 70, 2876 (1948).

55. Vogel, "A Textbook of Practical Organic Chemistry", Longmans Green, 1948.

56. F. Westheimer and N. Nicolaides, J. Am. Chem. Soc., 71, 25 (1949).

57. F. C. Whitmore and L. H. Sommer, J. Am. Chem. Soc., 68, 481 (1946).

58. K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 74, 6152 (1952).

59. K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 72, 5795 (1950).

60. K. E. Wilzbach, L. Kaplan and W. G. Brown, J. Am. Chem. Soc., 74, 1343 (1952).