3. Kinetical Study on the Reactivity of Organo-Silicon Compounds. (I)

The Cleavage Rate of Si-H Bond of Triethylsilane by HCl

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The cleavage of Si-H bond of hydrosilanes by the action of alkali has already been found by A. Stock and co-workers,[1] and F. P. Price[2] has also reported that the reaction rate of trialkylsilane with alcohol solvent was studied and that the cleavage of Si-H bond proceeded with a nucleophilic attack of hydroxyl ion.

On the other hand, the study on this cleavage reaction in the presence of acid has not yet been reported, beyond the discovery by Post[3] of the fact that the decomposition of trialkoxysilane was promoted in the presence of HCl.

As we found previously[4] that alkyl silanes were also decomposed by HCl easily in polar solvent, we performed this work to clarify kinetically the mechanism of this cleavage reaction of Si-H bond.

In this paper, the experimental results about the decomposition rate of triethyl-silane in the presence of HCl are reported[5].

EXPERIMENTAL

1. Preparation

Triethylsilane used in this investigation, was prepared by adding an appropriate amount of trichlorosilane to ethylmagnesium bromide. Its purity determined by the decomposition with sodium hydoxide was 99.5% and b. p. 107–108°C.[6]

· Ethyl alcohol was mainly used as the solvent. It was purified by the ordinary method and then carefully dried.

As alcohols other than ethyl alcohol, *n*-propyl alcohol and *n*-butyl alcohol were used, and benzene, acetone and dioxane were also used as solvents, and all these were purified in the ordinary way.

As the catalyst, HCl was used, which was refined and dried in gaseous state and then absorbed in solvents.

2. Experimental Method

The kinetical runs were made as follows by the apparatus shown in Fig. 1.

At first, the silane and solvent (alcohol) including a certain amount of HCl
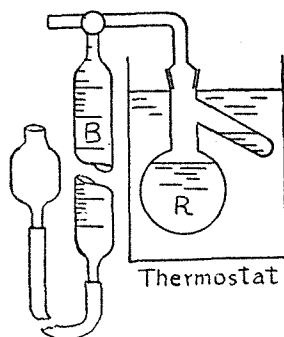
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Fig. 1.

were placed separately in the reaction tube R, and after attaining to the reaction temperature, both were mixed and the volume of gas, evolved with the progress of the reaction, was read by the attached burette B at regular intervals. The gas evolved in each run was mainly hydrogen (more than 97%), sometimes containing hydrocarbon but in small amount.

In the case of alcohol solvent, the total volume of gas evolved until the completion of the reaction was *ca.* 99% of the theoretical value calculated from the amount of silane, and the change of concentration of HCl in the reaction system was almost negligible throughout the reaction. Then it is considered that the main reaction in this case proceeds stoichiometrically as follows :

$$(Et)_3 \cdot SiH + HCl = (Et)_3 \cdot SiCl + H_2 \uparrow$$
$$(Et)_3 \cdot SiCl + ROH = (Et)_3 \cdot SiOR + HCl$$
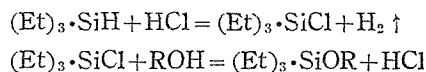
Accordingly, in the presence of excess alcohol, the amount of hydrogen evolved corresponds to that of the reacted silane.

The induction period was observed in the initial stage of the reaction under the condition of low concentration of silane at low temperature, but when powdered glass or KCl was added in the reaction tube, the induction period was so shortened as to become negligible. Though the nature of this induction period is not clear in detail, it is obvious that this is of heterogeneous nature. However, the main course of the reaction after the induction period was not affected by the addition of these compounds or by increasing the surface area of the reaction tube.

EXPERIMENTAL RESULTS

1. The Reaction Order for Silane

One example of the experimental results measured in the presence of HCl 2.1 *M* in ethyl alcohol is given in Table 1. The rate constants k_1 calculated as the first order reaction for the concentration of the silane remained almost satisfactorily constant up to about 60% completion.

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Table 1.

[Silane]$_0$: 1.373 M [HCl]$_0$: 2.10 M

in C$_2$H$_5$OH at 50°C

Time (min.)	Reaction %	k_1 (min.$^{-1}$)
0	0	—
5	5.15	0.0131
12.5	15.4	0.0132
17	20.6	0.0136
25	29.6	0.0140
33	36.8	0.0139
40	42.5	0.0139
55	51.3	0.0136
65	57.3	0.0131
81	64.3	0.0127
90	67.6	0.0125

Average value : 0.0133

Next, varying the concentration of silane within the range of 0.373 and 0.0933 M, we found the linear relation between log $\{V_F/(V_F-V_t)\}$ and t in each run, where V_F is the volume of gas evolved at completion of the reaction and V_t is that at the reaction time t, as shown in Fig. 2.
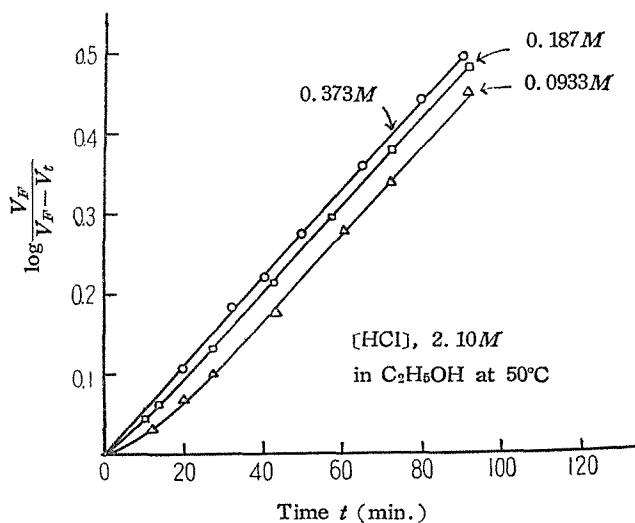

Fig. 2.

Owing to the difference in the length of the induction period, the position of the plotted straight lines shifted slightly, but those inclinations agreed well with each other, and the fixed first order rate constant was obtained from these incli-

nations.

Thus, the first order rate constants, k_1 at 40, 45 and 50°C were obtained respectively at the concentration of HCl 2.1 M and the activation energy E and the frequency factor A calculated by the Arrhenius equation are given in Table 2.

Table 2.

[HCl]$_0$: 2.10 M

[Silane]$_0$: 0.373–0.0933 M

Temp °C	k_1 (min.$^{-1}$)
40	0.00611
45	0.00878
50	0.0133
E (kcal./mole)	15.9
log A (min.$^{-1}$)	8.92

2. The Reaction Order for HCl

The relation between the first order rate constant, k_1, and the consentration of HCl, [HCl], in the range of 0.0425–2.10 M was investigated and the results are shown in Table 3.

Table 3.

[HCl]$_0$ (M)	* f 25°C	k_1 50°C (min.$^{-1}$)
0.0425	0.38	0.0000600
0.0850	0.31	0.000158
0.127	0.28	0.000255
0.170	0.27	0.000362
0.525	0.18	0.00112
1.05	0.15	0.00374
1.57	0.14	0.00770
2.10	0.13	0.0133

* f was calculated from γ at 25°C of H. Hartley[?].
This is scarcely affected by the temperature in the range of 20–40 °C, and thus it may be assumed that the activity coefficients of HCl in the reaction system under the condition of this experiment will be approximately equal to these values.

Now, the activity coefficient f of HCl in ethyl alcohol varies with its concentration as given in the 2nd column of Table 3, and then, under the consideration of such a change of the activity coefficients, we know that the reaction order for the activity of HCl is approximately of the 1.99th order from the plot of log k_1 against log ([HCl]$\times f$) as illustrated in Fig. 3. From this, it is deduced that the rate of this
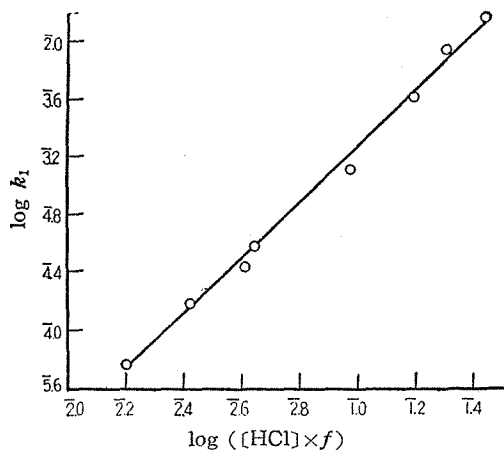
Fig. 3

reaction is proportional to the product of the activities of H^+ and Cl^- in the reaction medium in which HCl has been completely ionized.

3. The Influence of Solvent

The experimental results in some solvents are given in Table 4.

Table 4.

Effect of Solvent

Solvent	$[HCl]_0$ (M)	k_1 50°C $(min.^{-1})$ (initial)
Ethyl alcohol	1.05	0.00374
n- Propyl alcohol	1.05	0.00433
n-Butyl alcohol	1.05	0.00490
Ethyl alcohol 50% (vol.) +benzene 50%	1.05	0.00362
Ethyl alcohol 25% (vol.) +benzene 75%	1.05	0.00333
Benzene	0.10	no reaction
Acetic acid	6.0	no reaction
Dioxane	2.10	ca. 0.003
Acetone	2.10	ca. 0.64
Ethyl alcohol	2.10	0.0133
Ethyl alcohol 98% (vol.) +water 2%	2.10	0.0132

[Silane]₀ : 0.373 M

In cases of the alcohol solvents, the reaction rates were relatively large in n-butyl alcohol and less in n-propyl- and ethyl alcohol in that order, but the difference was not noticeable.

Effect of a small amount of water added to ethyl alcohol was negligible on the

rate.

In benzene–alcohol mixtures, the rate constants became smaller as the amount of benzene increased.

In the solvents other than alcohol, the concentration of HCl in the reaction system decreases as the reaction proceeds, therefore the solvent effect on the cleavage rate must be examined by comparing the initial specific rates in these solvents.

In pure benzene and in acetic acid which contained 0.1 M and 6.0 M of HCl respectively, silane hardly reacted with HCl, and also in dioxane the rate was very slow.

According to the report of F. Hall[5], the activity coefficient of HCl is small in acetic acid and increases in dioxane and in alcohol in that order, therefore variation of the activities of HCl in these solvent coincides qualitatively with the change of the rates of this reaction.

These results have revealed the fact that ionized HCl mainly takes part in the cleavage of Si-H bond of the silane.

In acetone, the reaction proceeded more rapidly than in ethyl alcohol, but most of the hydrogen produced was consumed for the reduction of acetone, and only a part of the hydrogen evolved in gaseous state.

It is very significant that the nascent hydrogen produced by this cleavage reaction is effective as the reducing agent.

The details of the reaction mechanism will be discussed in the next paper.

SUMMARY

The rates of the cleavage of Si–H bond of triethylsilane in the presence of HCl were measured in alcohol and in some other solvents.

In alcohol, this reaction rate was of the first order for the concentration of the silane, and the first order rate constant k_1 obtained at the concentration of HCl 2.1 M in ethyl alcohol was given by the following equation at the temperatures 40-50°C.

$$\log k_1 = 8.92 - 15900/4.5T \quad (1 /\text{min.})$$

This reaction rate in ethyl alcohol was approximately of the 1.99th order for the activity of HCl in it, and from this it was deduced that this reaction rate was proportional to the product of the activities of H+ and Cl-.

Moreover, from the comparison with the results in some other solvents, it was ascertained that ionized HCl mainly took part in this cleavage reaction.

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