STUDIES ON THE KINETICS OF THE REACTION OF ACETYLENE WITH AQUEOUS FORMALDEHYDE SOLUTION, II

By Ryo Kiyama, Jiro Osugi and Keizo Suzuki

In the previous work[1], the reactions between acetylene and formaldehyde at their earlier stage were studied, and the reaction mechanism was made clear. According to the mechanism, the establishment of the stationary concentration of propargyl alcohol may be expected as the reaction proceeds.

In the present work, therefore, the experiments of the long run are performed to reach the stationary concentration of propargyl alcohol, and the results obtained are discussed. Moreover, the studies on the problems which were not to be solved thoroughly in the previous work and some others are added.

Equilibrium Concentration in Propargyl Alcohol Formation

As made clear in the previous work, acetylene and the formed propargyl alcohol adsorb on the active point of the catalyst, and the adsorption power of the latter is smaller than the former, but with the increase of the formed amount of propargyl alcohol, propargyl alcohol adsorbs instead of the acetylene adsorbed on the active point of the catalyst, and then the adsorbed amount gradually increases with the increase of the concentration of propargyl alcohol. While the adsorbed propargyl alcohol reacts with formaldehyde to produce butynediol, and then the rate of propargyl alcohol formation balances with that of butynediol formation as the reaction proceeds. It is, therefore, considered that the formed amount of propargyl alcohol approaches to a definite concentration. Now, denote this value as the (apparent) equilibrium concentration in propargyl alcohol formation. The experiments are performed on the problem how this value and the time which is taken to reach equilibrium are changed by the pressure and the temperature of the reaction system, and the considerations are carried out on the results obtained.

Experimentals The experimental apparatus and its procedures are the same as in the previous work. But the amount of the catalyst used is about 60 cc, and as to the aqueous formaldehyde solution, 230 cc of the distillate of a commercial solution (B. P. 96 ~ 98°C) whose concentration is 39.6%, pH 2.73 and methanol content 11.8%, is used.

Experimental results As to the effect of pressure on the equilibrium concentration in propargyl alcohol formation, the experiments are performed in the cases of 20,

1) R. Kiyama, J. Osugi and K. Suzuki, *This Journal*, **22**, 22 (1952)

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30 and $40 kg/cm^2$ pressures at $120°C$ and the effect of temperature is examined at $110°$ and $120°C$ at $20 kg/cm^2$ pressure. These results are shown in Fig. 1 as the curves of propargyl alcohol formation (the formed amo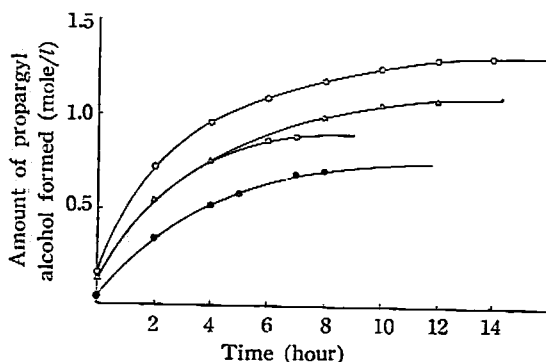unt of propargyl alcohol, mole/l, against time, hours). From any result obtained it is impossible to say that the perfect equilibrium concentration is attained within the time of experiment, but the values of approximate equilibrium are to be obtained by the extraporation on the curves. The equilibrium concentrations of propargyl alcohol and the times taken to reach equilibrium under various conditions are shown in Table 1.

As illustrated in Table 1, the equilibrium concentration increases and the time taken to reach equilibrium becomes longer as the pressure rises,

Fig. 1   Curves of propargyl alcohol formed

		temp. (°C)	press. (kg/cm²)
O	Exp. 60	120	40
△	Exp. 61	//	30
□	Exp. 58	//	20
●	Exp. 62	110	//

Table 1

Equilibrium concentration in propargyl alcohol formation and time taken

Exp. No.	Temperature (°C)	Pressure (kg/cm²)	Equilibrium concentration (mole/l, obs.)	Equilibrium * concentration (mole/l, calc.)	Time taken (hours)
60	120	40	1.32	1.31	14
61	//	30	1.10	1.11	12
58	//	20	0.90	0.95	8
62	110	//	0.75	0.80	8

* Described below

and also the former is higher at high temperature.

As shown in Fig. 2, moreover, the relations between the decreased amount of formaldehyde and time are linear within about 8 hours (where ca. 39% formaldehyde decreases to ca. 14%) and coincide regardless of the pressure with the results obtained in the previous work, but thereafter the relation deviate from the linearity.
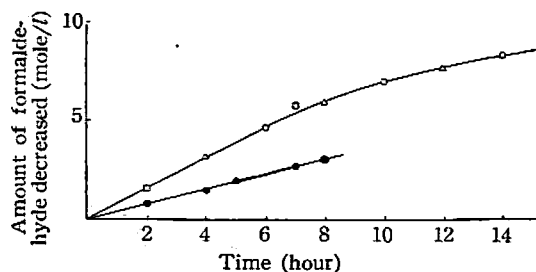

Fig. 2   Curves of formaldehyde decreased

		temp. (°C)	press. (kg/cm²)
O	Exp. 60	120	40
△	Exp. 61	//	30
□	Exp. 58	//	20
●	Exp. 62	110	//

Considerations In the previous work, the rate of propargyl alcohol formation can be expressed satisfactorily by the following equation,

$$\frac{d[P]}{dt} = k_2' - k_3[P]. \tag{1}$$

The relations between $\frac{d[P]}{dt}$ and [P] in the present experimental results, as shown in Fig. 3, are satisfactorily linear as shown in the previous work. Accordingly Eq. (1) holds, where rate constant k_2' may be considered to be related to the rate of decrease of formaldehyde consumed by the propargyl alcohol formation, and also k_3 related to the butynediol formation. Each value is obtained from the intercept in ordinate and the slope of the straight line shown in Fig. 3 as described previously.
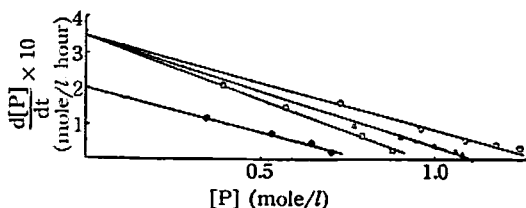

Fig. 3 Relations between $\frac{d[P]}{dt}$ and [P]

		temp. (°C)	press. (kg/cm²)
O	Exp. 60	120	40
△	Exp. 61	"	30
□	Exp. 58	"	20
●	Exp. 62	110	"

Taking into consideration the case where the propargyl alcohol formation reaches equilibrium, namely the formation rate $\frac{d[P]}{dt}$ becomes zero, from Eq. (1),

$$\frac{k_2'}{k_3} = [P]_e \tag{2}$$

is derived. That is, the equilibrium concentration of propargyl alcohol $[P]_e$ is obtained from the ratio of both rate constants. Let us consider qualitatively at first how the value of $[P]_e$ depends on the pressure and the temperature of the reaction system referring to Eq. (2).

In the case where the pressure is varied at a definite temperature (Exps. 58, 60 and 61), k_2' is constant and independent of the pressure, and k_3 decreases with the rise of pressure as shown in Fig. 3.   Consequently, $[P]_e$ should increase as the pressure rises.

When the temperature is varied at a definite pressure (Exps. 58 and 62), it is shown in Fig. 3 that the values of k_2' and k_3 are larger at high temperatures, but the temperature dependence of $[P]_e$ can not be known without the knowledge of the temperature coefficients of k_2' and k_3.   If the activation energies related to k_2' and k_3 are designated as E_2 and E_3, the following relation is derived from Eq. (2),

$$\frac{a'e^{-E_2/RT}}{ae^{-E_3/RT}} = Ae^{-(E_2-E_3)/RT} = [P]_e. \tag{3}$$

The values of E_2 and E_3 obtained from the relations of $\log k_2' - 1/T$ and $\log k_3 - 1/T$ in Exps. 58 and 62 are 16.0 and 11.5 kcal respectively, and so $E_2 - E_3 > 0$.[*]   There-

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[*]   The result that $E_2 - E_3 > 0$ coincides with the one in the previous work.

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fore, $[P]_e$ should be larger as the temperature rises.

The calculated values of $[P]_e{}^*$ obtained from Fig. 3 are shown in Table 1, which fairly coincide with the experimental results.

If the equilibrium concentration of propargyl alcohol is designated as $[P]_e'$ at temperature T', from Eq. (3)

$$\ln\frac{[P]_e}{[P]_e'} = -\frac{E_2 - E_3}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{4}$$

is derived. Substituting the values of the equilibrium concentration of propargyl alcohol obtained experimentally from Exps. 58 and 62 into Eq. (4), the value of $E_2 - E_3$ is 5.4 kcal, which almost coincides with 4.5 kcal described above.

From the considerations mentioned above, the validity of the rate equation (1) of propargyl alcohol formation and of the reaction mechanism described in the previous work is established.

As to the reason that the rate of decrease of formaldehyde gradually diminishes after about 8 hours, the change of the medium due to the reaction products and others should be examined, but it may be difficult to elucidate the reason clearly.

Concentration Effect of Formaldehyde on the Reaction Rate

In the previous work the concentration effect was discussed, but as described in the previous paper the solutions of known formaldehyde concentration which are pre-pared by the distillation of a commercial formaldehyde solution and diluted with distilled water are different from each other in methanol content and the pH value, and so it is impossible to obtain the sole effect of formaldehyde concentration. In the present experiment, therefore, the solution used is the filtrate of a commercial paraformaldehyde dissolved in boiling water. The 20.5 and 30.0% solutions are prepared by dilution with distilled water. But these samples have a slightly different pH values of 2.80 and 2.76 respectively. From the literature[2] that the depolymerization rate of formaldehyde polymer, however, hardly changes in the pH range $2.6 \sim 4.3$, it may be assumed that the results obtained in these experiments, which are shown in Fig. 4, show the con-centration effect only.

As shown in Fig. 4, the rate of formaldehyde decrease, propargyl alcohol and butynediol formation become larger as the initial formaldehyde concentration is high. This result is considered to be related to the fact that the depolymerization rate of formaldehyde polymer becomes larger as the initial formaldehyde concentration in-creases[2].

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* These values are directly obtained from the intercepts of abscissa in Fig. 3 if referred to Eq. (2).

2) M. Wadano, C. Tregus and K. Hess, *Ber.*, **67**, 174 (1934)

Medium Effect on the Activation Energies

It was estimated in the previous work that the values of the activation energies are affected by the differences of medium due to the methanol content, the pH value, etc. in an aqueous formaldehyde solution. The results obtained on this problem after the previous work are shown in Table 2.

The results of Sample Nos. 1 and 2 are taken from the experimental results of the formaldehyde concentration effect described above, and Sample No. 3 is prepared to a given concentration by addition of methanol and distilled water to the aqueous formaldehyde solution prepared from paraformaldehyde as mentioned above. The results of Sample No. 4 are taken from the equilibrium experiment of propargyl alcohol above described, where the samples are prepared with the distillate of a commercial formaldehyde solution are used.
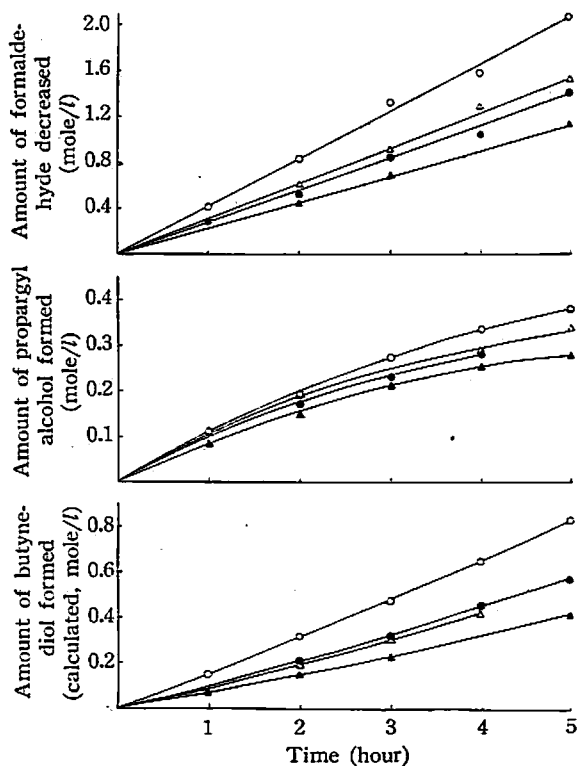

Fig. 4   Reaction curves of formaldehyde concentration effect

formaldehyde %

○	Exp. 74	30.0	at 120°C
△	Exp. 71	20.5	at 20kg/cm² pressure
●	Exp. 73	30.0	at 110°C
▲	Exp. 72	20.5	at 20kg/cm² pressure

Table 2

Activation energies under various conditions

Sample No.	Exp. No.	Temperature (°C)	Formaldehyde concentration (g/100 cc)	Methanol content (g/100 cc)	pH	Activation energy* (kcal)		
						E_1	E_2	E_3
1	71 72	120 110	20.5	0	2.80	8.7	5.2	4.3
2	73 74	110 120	30.0	0	2.76	12.5	10.1	6.6
3	75 76	120 110	20.2	5.7	3.52	20.5	13.9	10.0
4	58 62	120 110	39.6	11.8	2.73	22.6	16.0	11.5

* E_1, E_2 and E_3 are the activation energies related to the constants k_1', k_2' and k_3 respectively.

In Sample Nos. 1 and 2 in which the difference of the pH value is scarcely re-
cognized, the activation energies are larger in the latter, namely in the case of the
high concentration of formaldehyde. The formaldehyde concentration of Sample No.
3 is almost equivalent to that of Sample No. 1, but as the pH value is different from
the latter owing to the addition of methanol, it is impossible to discuss the effect of
the addition of methanol only. However, from the literature[2] that the depolymerization
rate of the formaldehyde polymer hardly changes in the pH range 2.6 ~ 4.3, it is con-
sidered that the addition of methanol is the chief cause to make the activation energy
large.   In Sample No. 4 which has the highest formaldehyde concentration and the
largest methanol content (the pH value being smallest), the largest activation energies
are obtained in comparison with the others.

　　Discussions on the sole effect described above are not to be made from the results
of Table 2, but it is obvious that the activation energies are affected by the differences
in the concentration and the medium of the aqueous formaldehyde solution used.
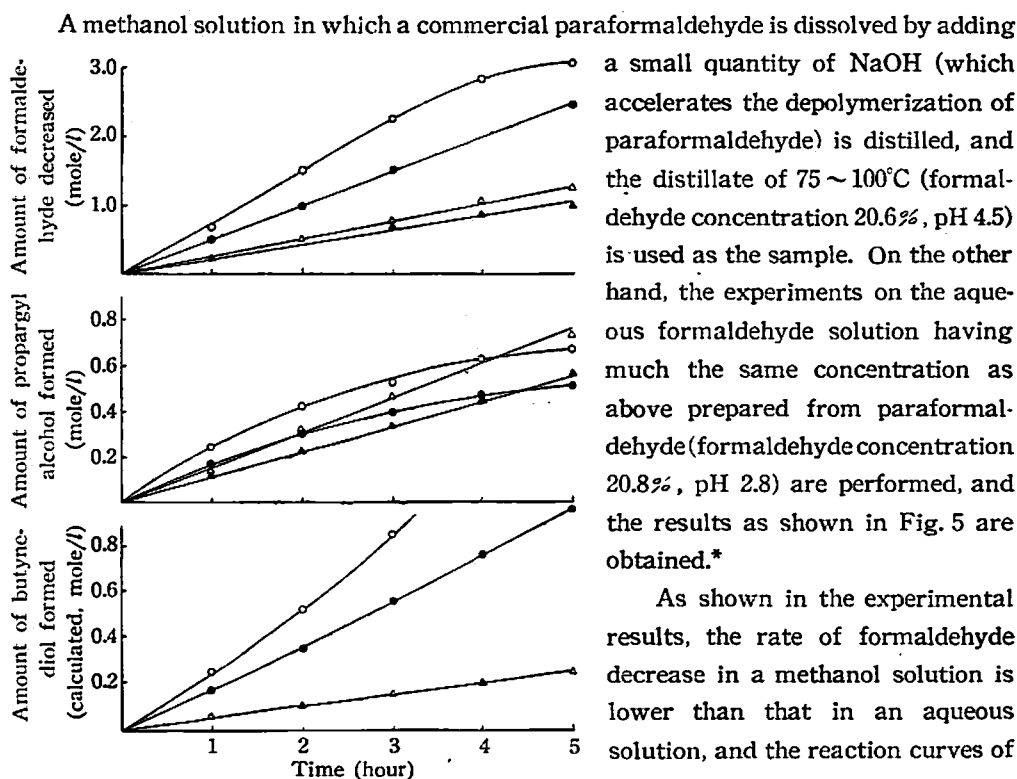
Reaction in Methanol Solution

A methanol solution in which a commercial paraformaldehyde is dissolved by adding
a small quantity of NaOH (which accelerates the depolymerization of paraformaldehyde) is distilled, and the distillate of 75 ~ 100°C (formaldehyde concentration 20.6%, pH 4.5) is used as the sample. On the other hand, the experiments on the aqueous formaldehyde solution having much the same concentration as above prepared from paraformaldehyde (formaldehyde concentration 20.8%, pH 2.8) are performed, and the results as shown in Fig. 5 are obtained.*

As shown in the experimental results, the rate of formaldehyde decrease in a methanol solution is lower than that in an aqueous solution, and the reaction curves of

Fig. 5　Reaction curves of methanol solution
　　　　and aqueous solution of formaldehyde

△　Exp. 81　methanol solution⎫at 120°C
○　Exp. 82　aqueous solution⎰at 20 kg/cm² pressure
▲　Exp. 80　methanol solution⎫at 110°C
●　Exp. 83　aqueous solution⎰at 20 kg/cm² pressure

* In the experiment in methanol
solution it is difficult to prevent thorough-
ly the evaporation of the materials in the
reaction vessel owing to the low boiling
temperature of the sample.

propargyl alcohol formation in the former is almost linear and its amount is larger than the latter as the reaction proceeds. The ratio of the butynediol and propargyl alcohol formed is greater than unity in an aqueous solution and smaller than unity in a methanol solution.

These results are explained from the reasons that the depolymerization rate of formaldehyde polymer is decreased in a methanol solution[2] and the solubility of acetylene into a methanol solution is higher.

Reaction between Propargyl Alcohol and Formaldehyde under Atmospheric Pressure

As made obvious in the previous work, butynediol is formed as follows, that is, the propargyl alcohol formed from acetylene and formaldehyde, adsorbs on the active point of the catalyst, while the formaldehyde polymers adsorbed on the carrier of the catalyst depolymerize to the monomer, which reacts with the adsorbed propargyl alcohol to form butynediol by the surface reaction. Therefore, butynediol synthesis should be possible from propargyl alcohol and formaldehyde in the presence of a catalyst without the supply of acetylene. Moreover, the activation energy in the butynediol formation from propargyl alcohol and formaldehyde is relatively small, and so the reaction is expected to occur at such a low temperature that the appliance of pressure is not needed. Then the following experiment under atmospheric pressure is performed.

Propargyl alcohol and a formaldehyde solution are boiled in a flask with a reflux condenser at 95 ~ 96°C (azeotropic temperature of propargyl alcohol and formaldehyde solution) under atmospheric pressure in the presence of the same active copper acetylide catalyst as used above. The samples taken out at a fixed time interval are analysed and the reaction curves shown in Fig. 6 obtained.

From the results which are obtained in the presence of relatively small amount of catalyst, it is shown that the amounts of propargyl alcohol and decrease of formaldehyde are seemingly linear against time, and by the distillation of the reaction products, butynediol is obtained. In the absence of the catalyst the reaction does not occur.
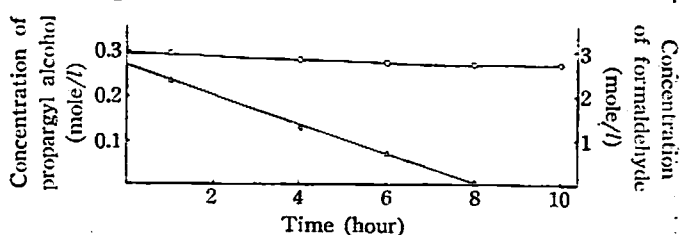

Fig. 6. Reaction curves between propargyl alcohol and formaldehyde

○ formaldehyde   △ propargyl alcohol

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