

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

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The reactions between acetylene and formaldehyde designated as "ethinylation", which was one of a series of the organic syntheses from acetylene of J. W. Reppe and coworkers, were studied. When the compressed acetylene gas is flowed continuously through an aqueous formaldehyde solution in the presence of a copper acetylide catalyst, the reactions occur as follows:



These reactions were studied from the stand point of chemical kinetics. The present report concerns to the earlier stage of the reaction.

Experimental Apparatus and Procedure.

The main part of the apparatus consists of an acetylene gas generator, a gas purifier, a compressor and a reaction vessel. The schematic layout of the apparatus is shown in Fig. 1.

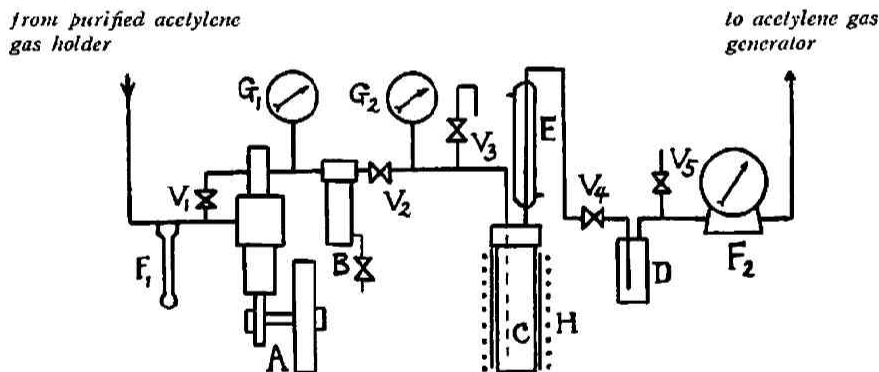


Fig. 1 Schematic layout of apparatus.

- A : Compressor of acetylene gas.
- B : Oil separator,
- C : Reaction vessel, volume about 320 cc (60 × 162 mm), which is lined with glass to prevent reaction products from being made dirty by corrosion of reaction vessel,
- D : Washing bottle,
- E : Reflux condenser for cooling.
- F₁, F₂ : Gas flow meters,
- G₁, G₂ : Burdon-type pressure gauges,
- V₁...V₄ : High pressure valves,
- V₅ : Glass stop cock,
- H : Electric heater. The temperature of reaction vessel is measured by means of a thermocouple inserted inside the vessel.

The experimental procedures are as follows: The air in the reaction system is completely replaced with acetylene gas. The confirmation is made by analysis of the gas sample taken through the glass cock V_6 . Then valve V_4 is closed and after the reaction system reaches a given pressure by compression of acetylene, valve V_7 is closed. When the reaction vessel is heated to a given reaction temperature, acetylene gas is made to flow under constant pressure by opening valve V_2 and regulating valve V_4 . The beginning of the flow is taken as the start of reaction, and the samples of reaction products at each given time interval are taken out through valve V_3 after closing valves V_4 and V_2 . The amount of acetylene gas drawn by a compressor is regulated by return valve V_1 , observing differential flow meter F_1 .

The evaporation of the materials in the reaction vessel is almost completely prevented by reflux cooling condenser E. The discharged acetylene gas, the amount of which is measured by gas flow meter F_2 , returns to the gas generator and is recycled.

Catalyst.

The catalyst of copper-bismus is used. Electrolyzed metallic copper and metallic bismus in ratio of 4 parts to one are dissolved as nitrates with conc. nitric acid and the nitrates are adsorbed with silica gel. After excessive nitric acid and water is removed by heating at $280 \sim 300^\circ\text{C}$, the silica gel adsorbed is roasted for about 2 hours at 500°C by occasional stirring.

To convert to active copper acetylide, the catalyst and an aqueous formaldehyde solution are brought into an autoclave, and shaken at $70 \sim 100^\circ\text{C}$ after 20 kg/cm^2 acetylene gas is charged. This procedure is repeated and carried out for about 20 hours in all. Thus, the active catalyst obtained is employed in the experiment, but the catalyst is required to use further in the experimental process mentioned above about 50 hours to secure the reproducibility of experimental results. The catalyst is hung in the basket made of copper net in the reaction vessel lined with glass. After the reaction finishes, the catalyst, being taken out, is washed thoroughly with an aqueous methanol solution and distilled water to remove the materials adsorbed on the catalyst, and is stored in a dilute aqueous formaldehyde solution. By the procedures the activity of the catalyst is kept constant. The experimental results are compared and discussed referring the same activity of the catalyst.

Preparations and Analyses of Experimental Materials.

(1) Acetylene gas.

Acetylene gas prepared with calcium carbide and water is purified through a dry refining reagent, and stored in a gas holder. Any acidic substances are removed with the second purifier containing $30 \sim 40\%$ aqueous potassium hydroxide solution.

In the gas analysis by means of Hempel's apparatus, the amount of acetylene is determined with either a fuming sulphuric acid, an alkaline potassium mercuric iodide solution or bromine water, and that of oxygen with an alkaline pyrogallol or sodium hyposulphite solution as absorbent.

The purities of acetylene gas are constant throughout the experiments: acetylene, 99.6~99.4 %, oxygen, below 0.1 %.

Of the residual gases, hydrogen sulphide is examined and the amount contained is below the detection limit (0.0033 %). Traces of phosphine are qualitatively detected.

(2) Aqueous formaldehyde solution.

The distillate of commercial formaldehyde solutions at 96~98°C (pH about 2.7, about 10 % methanol contained) is diluted to required concentrations with distilled water. 250 cc of an aqueous formaldehyde solution is used in one experiment. The sodium sulphite method⁽¹⁾ is applied in formaldehyde analysis. The sodium hydroxide stoichiometrically liberated according to the following chemical equation, is titrated with the known hydrochloric acid in the presence of thymolphthalein as an indicator.



Analyses of Reaction Products.

(1) Propargyl alcohol.

Propargyl alcohol precipitates as a white crystal ($\text{AgC}\equiv\text{CCH}_2\text{OHAgNO}_3$) with known silver nitrate solution (about 0.1 N) in the presence of potassium acetate, and excessive silver nitrate is back-titrated with ammonium thiocyanate using iron alum acidified with nitric acid as an indicator. The percentage of propargyl alcohol is calculated from the amount of silver nitrate consumed.⁽²⁾

In order to confirm the analytical method described above, spectroscopic analysis was performed.* As shown in Fig. 2, the absorption of propargyl alcohol has a maximum near 2800 Å, while the absorption of aqueous formaldehyde is negligibly small. As a blank test, the relation between the concentrations of propargyl alcohol solution, containing formaldehyde, which are obtained by the distillation of the reaction products and determined by the silver nitrate method, and the extinction of the solutions is examined. The linear relation is obtained as shown in Fig. 3, which shows the reliability of the

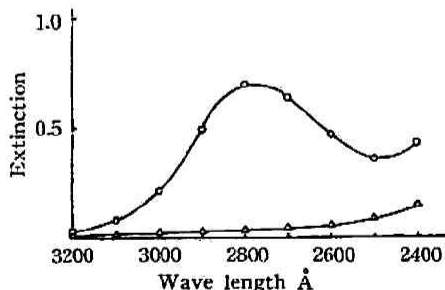


Fig. 2 Absorption of propargyl alcohol ○ and formaldehyde △.

(1) J. F. Walker, *Formaldehyde*, p. 257 (1944)

(2) J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, p. 107 (1949)

* By Beckman's Spectrophotometer imported by the Department of Education.

silver nitrate method regardless of the presence of formaldehyde. Moreover, butynediol does not react with silver nitrate, and then the presence has no influence on the analysis of propargyl alcohol.

(2) Butynediol-1, 4.

A given quantity of the reaction product is dried in evacuation to vaporize formaldehyde, propargyl alcohol and water, and residual is taken as butynediol. In the residual, the iron produced from corrosion of the reaction vessel is contained, but it is shown from the spectroscopic absorption that the iron contents in the samples are nearly constant. Accordingly, the relative amounts of butynediol in the samples can be obtained by this method.

Butynediol is found to have the absorption in the ultra-violet region, and the maximum is near 2700 Å as shown in Fig. 4. The relation between the concentrations and extinctions of butynediol is shown in Fig. 5. The total extinction of the reaction

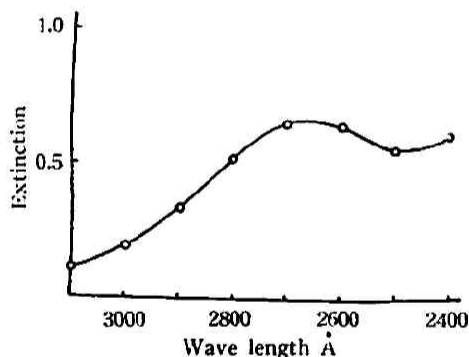


Fig. 4 Absorption of butynediol.

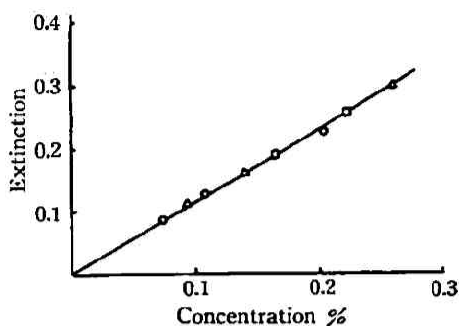


Fig. 3 Extinction-concentration of propargyl alcohol at 2800 Å.

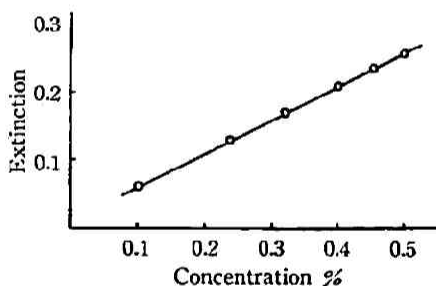


Fig. 5 Extinction-concentration of butynediol at 2800 Å.

products which is the sum of extinction of propargyl alcohol and butynediol is measured, and the extinction corresponding to the concentration of propargyl alcohol determined by the silver nitrate method is reduced from the total. The concentration of butynediol is then determined from the residual extinction in use of Fig. 5. But it is difficult to bring to a constant state the iron produced by the corrosion and contained in the reaction products, and so it is difficult to measure accurately the absorption caused by the iron. Therefore, accurate determination by this method is difficult to perform, but when the results are compared with the drying method mentioned above, it is confirmed that the reaction of acetylene with formaldehyde in the presence of a thoroughly active catalyst stoichiometrically produces propargyl alcohol and butynediol. Therefore, the analysis of butynediol is not performed at each experiment, and the amount of butynediol is calculated stoichiometrically from

the decreased amount of formaldehyde and the formed amount of propargyl alcohol

Experimental Results.

The experiments are performed in the ranges of $90 \sim 130^\circ \text{C}$, and $5 \sim 30 \text{ kg/cm}^2$ pressure, and the flow rate of acetylene gas is $2 \sim 3 \text{ l/min}$. The catalyst used is contained 12.3 % Cu and 3.2 % Bi which are adsorbed on a silica gel carrier. The total volume of the catalyst is about 40 cc.

The changes of reaction processes when temperature, pressure, formaldehyde concentration, methanol content, pH, etc. are changed, are investigated respectively. The experimental results obtained are classified and described according to the above mentioned experimental variables which are designated as the effect. The decreased amount of formaldehyde, the formed amount of propargyl alcohol and that of butynediol against time are illustrated in each effect. These are shown in Figs. 6 ~ 10. The experimental conditions are noted respectively in the figures.

(1) Temperature effect.

As shown in Fig. 6, the amounts decreased of formaldehyde, and those formed of propargyl alcohol and butynediol show increase as temperature rises. It is noticeable that the formaldehyde concentrations decrease linearly against time. This result

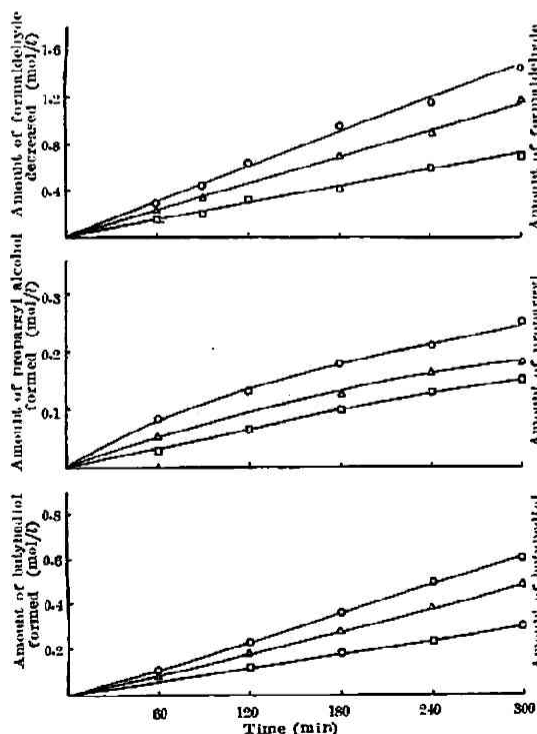


Fig. 6 Reaction curves of temperature effect.

○ Exp. 42 120°C
 △ Exp. 36 110°C
 □ Exp. 41 100°C

10 % formaldehyde
 at 10 kg/cm^2 pressure

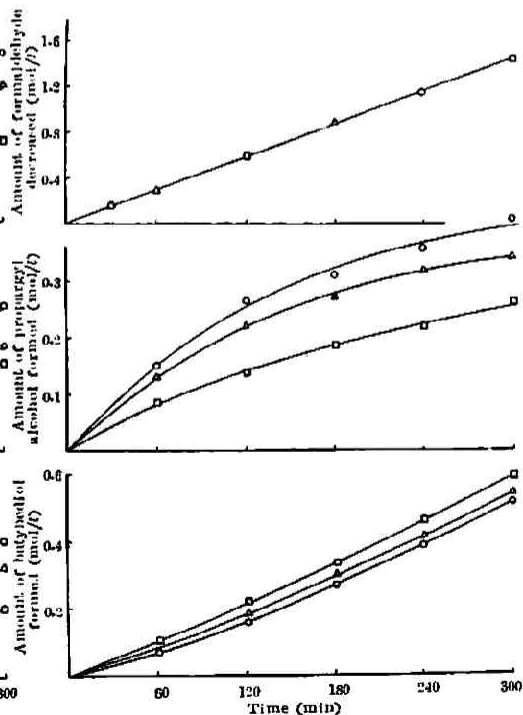


Fig. 7 Reaction curves of pressure effect.

○ Exp. 47 30 kg/cm^2
 △ Exp. 48 20 kg/cm^2
 □ Exp. 42 10 kg/cm^2

10 % formaldehyde
 at 120°C

is a common fact under the experimental condition, especially when the concentration of formaldehyde does not change largely.

(2) Pressure effect.

The effect is shown in Fig. 7. The rates of decrease of formaldehyde are constant independently of pressures, and the formed amount of propargyl alcohol increases as pressure rises. The amount of the formed butynediol, therefore, decreases with rising pressure.

(3) Formaldehyde concentration effect.

The 35 % formaldehyde solution used is obtained by distillation of a commercial solution (B.P. 96~98°C). The distillate contains about 10 % methanol and its pH is about 2.7. While a 10 % formaldehyde solution is the one which is obtained by the dilution of the above mentioned 35 % solution with distilled water, and then the methanol content is about 3 %, and pH about 3.0. Therefore, even if the result is designated as the formaldehyde concentration effect, it is dependent not only on the change of the formaldehyde concentration but also on the changes of the methanol

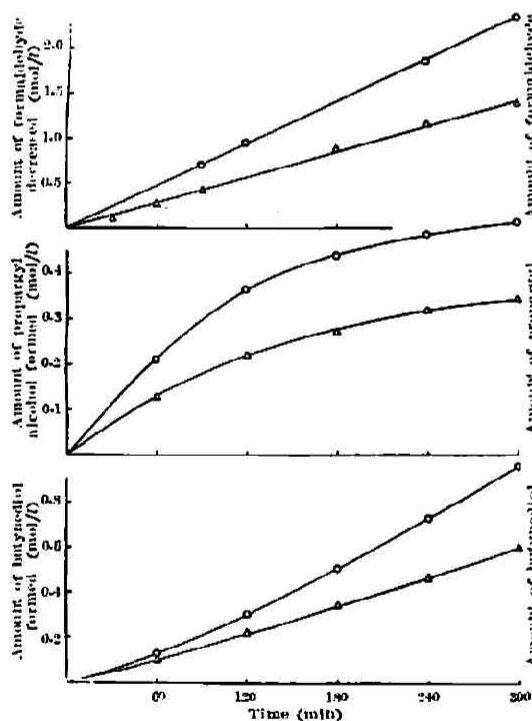


Fig. 8 Reaction curves of formaldehyde concentration effect.

○ Exp. 45 35 % formaldehyde } at 120°C
 △ Exp. 48 10 % " } at 20 kg/cm² pressure

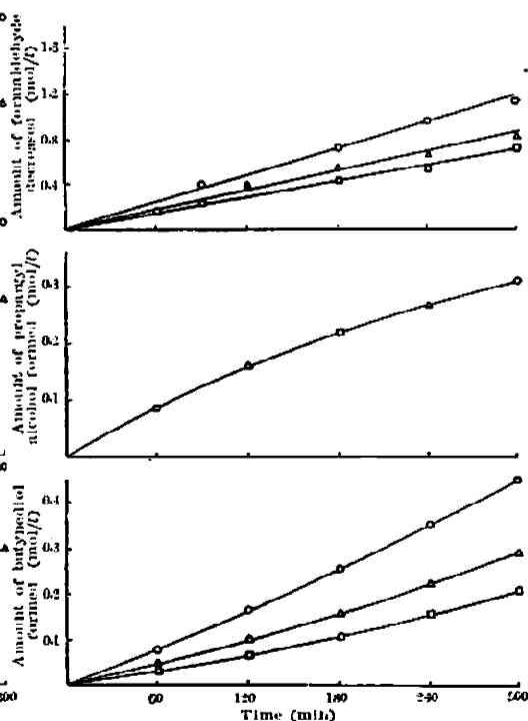


Fig. 9 Reaction curves of methanol effect.

methanol %
 ○ Exp. 40 3.4 } 10 % formaldehyde
 △ Exp. 43 6.5 } at 110°C
 □ Exp. 44 10.8 } at 20 kg/cm² pressure

content and pH. For convenience' sake, the results obtained are shown in Fig. 8 as the formaldehyde concentration effect. The amount of decrease of formaldehyde, and

the formed amount of propargyl alcohol and butynediol show considerable increase with the increase of formaldehyde concentration.*

(4) Methanol effect.

As shown in Fig. 9, where the reaction temperature is 110°C , the amount of decrease of formaldehyde falls with increase of the methanol content contained, but the amount of the propargyl alcohol formed nearly coincides. Accordingly, the amount of butynediol shows decrease with increase of the methanol content. But as for the amounts of formaldehyde decreased and the propargyl alcohol and butynediol formed at 120°C , the results in which 3.4% methanol is contained, if compared, almost coincides those in which 10.8% methanol is contained.

(5) pH effect.

The results obtained are shown in Fig. 10, where the solution designated as pH

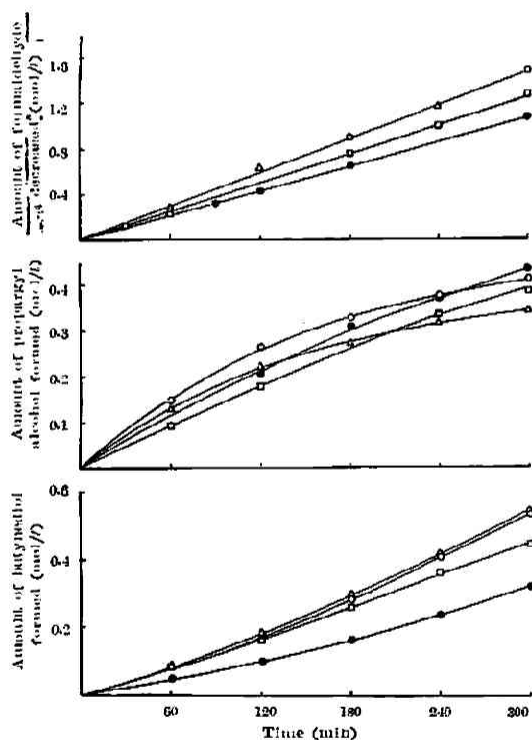


Fig. 10 Reaction curves of pH effect.

	pH	
○ Exp. 50	5.0 (NaOH)	10% formaldehyde at 120°C at 20 kg/cm^2 pressure
△ Exp. 48	3.0	
□ Exp. 49	1.7 (HNO_3)	
● Exp. 51	1.5 (HCOOH)	

increase of pH value in the range of 1.5~3.0. As the pH effect changes owing to

3.0 is the one which is prepared by diluting the original distillate of a commercial formaldehyde solution to 10% with distilled water, and that of pH 1.5 with formic acid, pH 1.7 with nitric acid and pH 5.0 with sodium hydroxide are prepared.

The smaller the pH value is, the less the amount of decrease of formaldehyde becomes. However, there is little difference between pH 3.0 and 5.0 and somewhat more in the latter. It is remarkable that the curves of propargyl alcohol formed against time are straight in 1.5 and 1.7 in comparison with 3.0 and 5.0. Then in the amount of the propargyl alcohol formed, the former two cases which have smaller pH values predominate over the latter as the reaction proceeds. The amount of butynediol formed increases with

* It must be remembered in this case that the rates of depolymerization of formaldehyde polymer in solution (mentioned below) are changed by the concentrations of starting solutions. cf. M. Wadano, *J. Electrochem. Assoc. Japan*, **14**, 61 (1946).

the reaction temperature, it is difficult to consider the effect indiscriminately, and there will be the effect due to the nature of material added. However, it is recognized at least that the fraction of propargyl alcohol in the reaction products is to be increased when the pH value is diminished with the addition of acidic materials.

Kinetical Discussions on the Experimental Results.

As shown in the experimental results, the curves showing the amount of decrease of formaldehyde are linear against time. Namely, the rates of the decrease are constant, and so the reaction is zero order. Moreover, it is found that the formaldehyde concentration does not decrease and the desorption of formaldehyde adsorbed occurs at the initial step (within 30 minutes) notwithstanding the progress of the reaction (especially when the reaction temperature is low and the formaldehyde concentration high). From these results it is considered that formaldehyde adsorbs on the surfaces of the wall of reaction vessel, the carrier of the catalyst, etc. and it is consumed by the surface reaction to the propargyl alcohol and butynediol. And then from the reason that adsorption rate of formaldehyde is fast in comparison with the reaction rate, it is seen that the reaction rate becomes zero order. Namely, the rate of decrease of formaldehyde is expressed as follows:

$$-\frac{d[F]}{dt} = k_1 \theta_f = k_1', \quad (1)$$

where $[F]$ is the concentration of formaldehyde in a solution, k_1 the rate constant and θ_f the fraction of formaldehyde adsorbed on the catalyst surface. θ_f can be regarded as constant within the change of the concentration of formaldehyde during the progress of the reaction. Accordingly, the rate of decrease of formaldehyde concentration is constant. Then, the experimental result that the rate is independent of the pressure, that is, of the concentration of acetylene, supports Eq. (1) described above. However, as shown in the experimental results, $k_1 \theta_f$ changes with temperature, pH, methanol content, etc.

Now the rates of formaldehyde decrease are measured at different temperatures, and the relations between the logarithm of k_1' obtained from the slope and $1/T$ are linear as shown in Fig. 11. From the relations, ca. 12 kcal is obtained as the apparent activation energy. The energy of depolymerization of formaldehyde polymer is about 17.4 kcal⁽³⁾, and so it is reasonable to assume that the value of activation energy, ca. 12 kcal con-

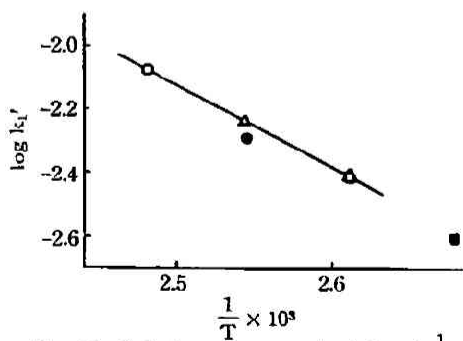


Fig. 11 Relations between $\log k_1'$ and $\frac{1}{T}$
 ○ Exp. 32 } 20 % formaldehyde
 △ Exp. 27 } at 10 kg/cm² pressure
 □ Exp. 28 }
 ▲ Exp. 42 } 10 % formaldehyde
 ● Exp. 36 } at 10 kg/cm² pressure
 ■ Exp. 41 }

(3) M. Wadano, C. Trogus and K. Hess, *Ber.*, 67, 174 (1934)

cerns to the depolymerization if the adsorption heat is taken into consideration. Therefore, it is considered that the process in which the polymer molecule depolymerizes to the monomer determines the rate of formaldehyde decrease.

The rate of propargyl alcohol formation at initial stage may be assumed to be expressed by the following equation.

$$\frac{d[P]}{dt} = k_2 \theta_f \theta_A = k_2' \frac{b[A]}{b[A] + b'[P]}, \quad (2)$$

where

$$\theta_A = \frac{b[A]}{b[A] + b'[P]}, \text{ and } k_2 \theta_f = k_2'.$$

In Eq. (2), θ_f which is the fraction of the formaldehyde adsorbed on the carrier of the catalyst may be regarded as constant and k_2' , therefore, is constant. Also θ_A expresses the fraction of the acetylene adsorbed on the active point of the catalyst. The reason that θ_A is expressed as in the above equation is based on the assumption that either acetylene or propargyl alcohol formed adsorbs on the active point of the catalyst. b and b' are the adsorption constants which depend on the adsorption power. When Eq. (2) is integrated by taking the initial concentration of acetylene in the solution to be a and the concentration of propargyl alcohol formed x , the following equation is obtained.

$$\frac{ab'}{b-b'} \cdot \frac{1}{t} \ln \frac{a}{a-x} = \frac{k_2' b}{b-b'} + \frac{x}{t}. \quad (3)$$

Substituting as

$$k_a = \frac{1}{t} \ln \frac{a}{a-x} \text{ and } v = \frac{x}{t},$$

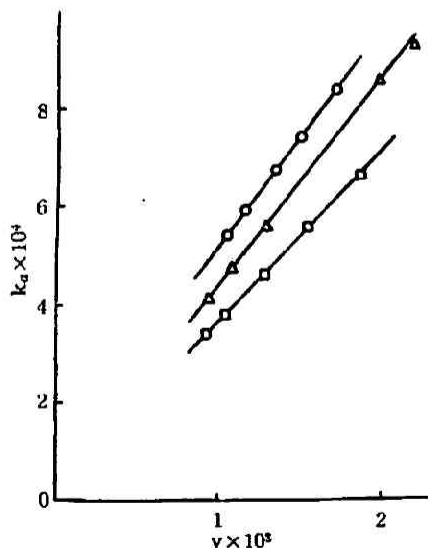


Fig. 12 Relations between k_a and v at different temperatures.

- Exp. 32 130°C } 10 % formaldehyde
 △ Exp. 27 120°C }
 □ Exp. 28 110°C } at 10 kg/cm² pressure

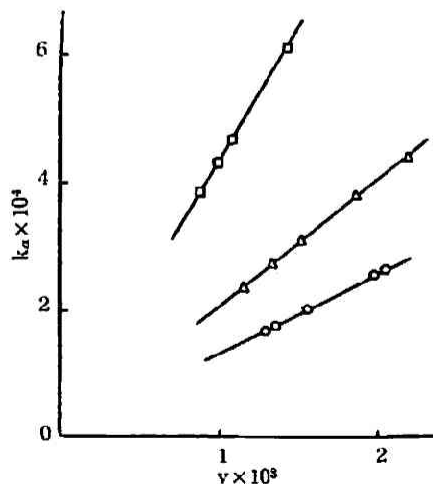


Fig. 13 Relations between k_a and v at different pressures.

- Exp. 42 10 kg/cm² } 10 % formaldehyde
 △ Exp. 48 20 " }
 □ Exp. 47 30 " } at 120°C

and plotting k_a against v , the linear relations always hold as shown in Figs. 12 and 13. That is, the relation of Eq. (3), therefore that of Eq. (2) is satisfied, and it is recognized that the above mentioned assumption is valid. The initial concentration of acetylene a i.e. the solubility under the reaction pressure is obtained, assuming the Raoult's law, from the hypothetical vapour pressure calculated at reaction temperature.

The change of the first term in the right side of Eq. (3) with temperature gives, assuming that b and b' do not change with temperature, the apparent activation energy of k_2' as 6~7 kcal. But it is difficult to obtain the accurate value of the activation energy by this method. Moreover, in Eq. (3) the relation $\frac{k_2'b}{b-b'} > 0$ or $b > b'$ is derived from Figs. 12 and 13. Namely, it is found that the adsorption constant of acetylene is larger as compared with that of propargyl alcohol.

Considering that θ_P is the fraction of the propargyl alcohol adsorbed on the active point of the catalyst and $\theta_A + \theta_P = 1$, Eq. (2) is rearranged as follows:

$$\frac{d[P]}{dt} = k_2 \theta_P (1 - \theta_P) = k_2' \left(1 - \frac{b'[P]}{b[A] + b'[P]} \right), \quad (4)$$

where

$$\theta_P = \frac{b'[P]}{b[A] + b'[P]}.$$

Assuming $b[A] \gg b'[P]$ as above described, and $[A]$ is constant from the experimental condition of constant flow, Eq. (4) reduces to

$$\frac{d[P]}{dt} = k_2' - k_3[P], \quad (5)^*$$

where k_2' is regarded to relate the decrease of formaldehyde concentration consumed by the propargyl alcohol formation and $k_3[P]$ the formation rate of butynediol. The exact meanings of k_2' and k_3 are difficult to define.

In order to examine whether Eq. (5) is satisfied or not, the relations between $\frac{d[P]}{dt}$ and $[P]$ are shown graphically from the experimental results. As shown in Figs. 14 and 15, the linear relations are obtained and it is confirmed that the above

* The same equation as Eq. (5) also holds even if included the decrease of propargyl alcohol by the butynediol formation:

$$\begin{aligned} \frac{d[P]}{dt} &= k_2 \theta_P \theta_A - k_3' \theta_P \theta_P, \\ &= k_2 \theta_P \frac{b[A]}{b[A] + b'[P]} - k_3' \theta_P \frac{b'[P]}{b[A] + b'[P]}. \end{aligned}$$

Assuming $b[A] \gg b'[P]$,

$$\frac{d[P]}{dt} = k_2 \theta_P - k_3' \theta_P \frac{b'[P]}{b[A]}.$$

and assuming $b[A] = \text{constant}$,

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

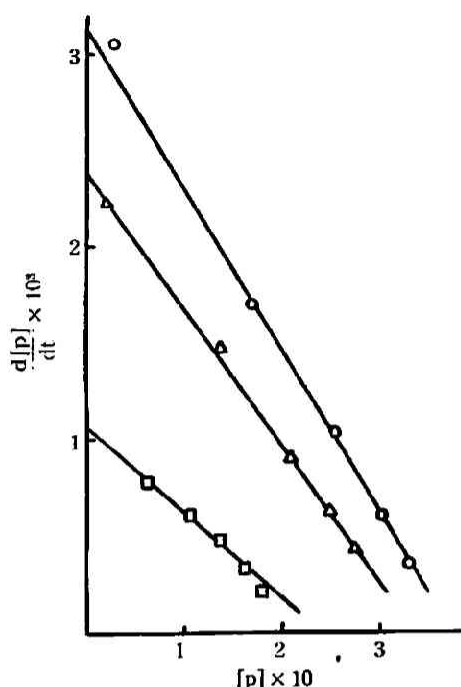


Fig. 14 Relations between $\frac{d[p]}{dt}$ and $[p]$ at different temperatures.

○ Exp. 27 120°C } 20 % formaldehyde
 △ Exp. 28 110°C }
 □ Exp. 29 90°C } at 10 kg/cm² pressure

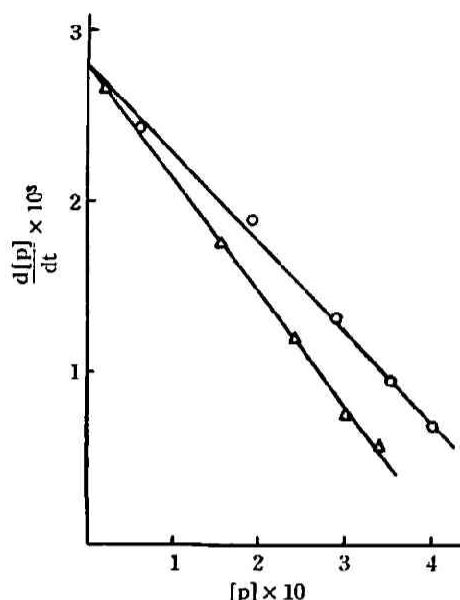


Fig. 15 Relations between $\frac{d[p]}{dt}$ and $[p]$ at different pressures.

○ Exp. 47 30 kg/cm² } 10 % formalde-
 △ Exp. 48 20 " } hyde at 120°C

assumptions are proper. Obtaining k_2' and k_3 respectively from the intercepts and the slopes in Fig. 14, the activation energy, as shown in Figs. 16 and 17, related to

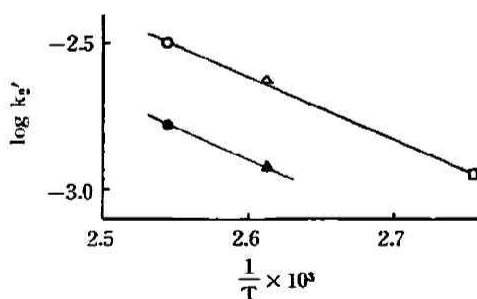


Fig. 16 Relations between $\log k_2'$ and $\frac{1}{T}$.

○ Exp. 27 } 20 % formaldehyde
 △ Exp. 28 }
 □ Exp. 29 } at 10 kg/cm² pressure
 ● Exp. 42 } 10 % formaldehyde
 ▲ Exp. 36 } at 10 kg/cm² pressure

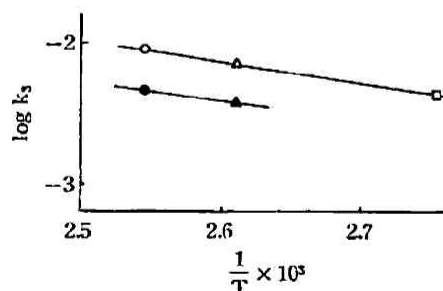


Fig. 17 Relations between $\log k_3$ and $\frac{1}{T}$.

○ Exp. 27 } 20 % formaldehyde
 △ Exp. 28 }
 □ Exp. 29 } at 10 kg/cm² pressure
 ● Exp. 42 } 10 % formaldehyde
 ▲ Exp. 36 } at 10 kg/cm² pressure

the process of the decrease of formaldehyde caused by propargyl alcohol formation k_2' is 8~9 kcal, and that of butynediol formation k_3 about 5 kcal.

The relations of Eq. (5) at the same temperature and at different pressures are shown in Fig. 15 and linear relations are also obtained. From the figure, it is found that k_2' is nearly coincident regardless of the pressure and k_1 decreases with rising pressure.

The apparent activation energies obtained are as follows:

$$E_1 = \text{ca. } 12 \text{ kcal related to } k_1',$$

$$E_2 = \text{ca. } 8 \text{ kcal related to } k_2',$$

$$E_3 = \text{ca. } 5 \text{ kcal related to } k_3.$$

These activation energies become nearly constant values in both 10 % and 20 % formaldehyde solutions notwithstanding the differences of methanol content, pH, etc. But it is estimated that these values are affected by the medium, which we shall mention in the future work.

Of the activation energies of various processes, that of the formaldehyde concentration decrease is the largest. It is considered that the reaction rate, over all, is governed by the rate of depolymerization of the formaldehyde polymer adsorbed.

Conclusions.

Summarizing the above kinetical results, the reaction mechanism is considered as follows. The acetylene molecule adsorbed on the active point of the catalyst reacts with the formaldehyde depolymerized from the polymer in the adsorbed state, and then propargyl alcohol is formed. The propargyl alcohol formed becomes free by desorption, but some propargyl alcohol adsorbs on the active point of the catalyst, and then reacts with formaldehyde to produce butynediol. The adsorption constant of acetylene on the active point is greater than that of propargyl alcohol, but as the concentration of propargyl alcohol becomes rich, the active point occupied by propargyl alcohol increases and so the rates of propargyl alcohol formation and of consumption due to butynediol formation are balanced and the stational concentration of propargyl alcohol is established.

The rate determining step of these reactions is the depolymerization of the formaldehyde polymer adsorbed, and the depolymerization rate changes with reaction temperature, pH, methanol content, etc. And from the reason that the adsorption rate of formaldehyde is greater than the reaction rate, the rate equation of formaldehyde decrease is found to be zero order.

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