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Kinetics of Copper(I)-Catalyzed Dimerization and Hydration of Acetylene in Water

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The kinetics of the dimerization and hydration of acetylene in water with a copper(I) catalyst, a so-called Nieuwland catalyst, were investigated. The stationary state kinetics for both reactions could be described assuming that the rate-controlling step is a second-order reaction of an activated catalyst, [H$\cdots$Cl–Cu–C_2H], formed in the reaction mixture, with acetylene or water. The activation energies and activation entropies were 12.4 $\mathrm{kcal \cdot mol^{-1}}$ and -33.3 $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$ for the acetylene dimerization, and 17.5 $\mathrm{kcal \cdot mol^{-1}}$ and -34.2 $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$ for the acetylene hydration, respectively. The large negative values of activation entropy for these reactions may be accounted for by the role of water as a kind of cocatalyst.

The dimerization of acetylene to vinylacetylene (MVA) in water catalyzed by cuprous salts, Nieuwland catalyst of CuCl/(KCl or NH_4Cl), is long-standing, but still one of the important industrial reactions.[1–4] MVA is now produced world wide (about 30000 metric-ton-per-year) as an intermediate product for chloroprene rubber based upon a process using acetylene as a starting material.[5] The introduction of acetylene into the reaction mixture results not only in the formation of MVA, but also in the formation of side products, such as acetaldehyde (ACH), by hydration,[6–15] divinylacetylene ($CH_2{=}CHC{\equiv}CCH{=}CH_2$: DVA)[1] and acetylenedivinyl ($HC{\equiv}CCH{=}CHCH{=}CH_2$: ADV),[1] both through trimerization. Although the catalyst was discovered by Nieuwland in the early 1930s, the catalytic reaction involves the latest topics in chemistry, that is, the mechanism of organic reactions in water. Recently, many new organic reactions, which could not occur in organic solvents, have been found to take place in water.[16] Although considerable attention has been focused on the mechanism of dimerization by the Nieuwland catalyst, nothing about the role of water in the reaction has been reported.[17–22] This paper presents the results of kinetic studies of both the dimerization and hydration of acetylene with the Nieuwland catalyst in water as well as the reasoning that water molecules may directly contribute to the catalyst mechanism.

Results and Discussion

Although the solubility of CuCl alone is as low as 236 ppm at 25 °C in water, by virtue of the presence of KCl, CuCl is dissolved in hot water (70 °C) in such a high concentration as about 5.5 $\mathrm{mol \cdot L^{-1}}$, extremely high as a "catalyst" concentration. Another noteworthy behavior is the absorption of acetylene into the reaction mixture, as shown in Fig. 1. The absorption of acetylene does not follow Henry's law, namely the amount of acetylene absorption does not converge to zero when the partial pressure of acetylene becomes zero. This abnormality may be accounted for by the combination of the mere absorption of acetylene and the production of a copper acetylide, as shown in Scheme 1. Since the exothermic reaction together with an abrupt decrease in the pH was observed just after starting the introduction of acetylene into the reaction mixture, copper acetylide seems to be produced immediately by introducing acetylene.[22] Copper acetylide formation must be very fast, and thus the quantity of acetylene absorption shows a plus value

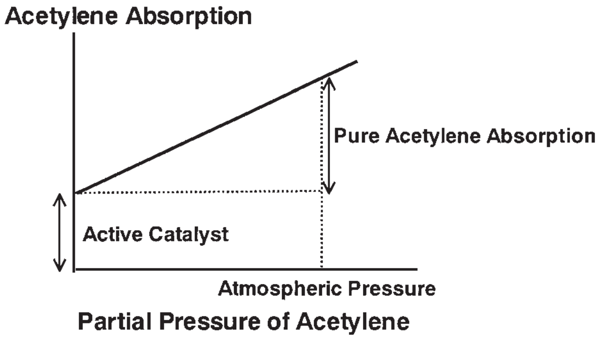

Fig. 1. A schematic diagram for the pressure dependence of acetylene absorption.

$$C_2H_2 + CuCl \longrightarrow [H...ClCu\text{-}C_2H] \xrightarrow{C_2H_2} CH_2CHC_2H + CuCl$$

Scheme 1.

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even when the partial pressure of acetylene is interpolated to zero. The value of the intercept may be taken as the concentration of the copper acetylide, expressed as "activated catalyst" in this paper. Furthermore, the pure concentration of acetylene can be estimated from the amount of acetylene absorption and the concentration of activated catalyst, as shown in Fig. 1. In this analysis, we presumed that the concentration of the activated catalyst is constant. The reasons are as follows: 1) The copper acetylide as an activated catalyst is immediately hydrated under a low-pH condition, and back to the acetylene molecule and the polymeric ate-complexes with CuCl–KCl;[22] 2) the rate of the AC dimerization is slower than that of hydration of the activated catalyst;[22] 3) the relationship between the partial pressure of acetylene and the acetylene absorption is linear in our experimental condition. The relationships between the partial pressure of acetylene and the concentration of acetylene in the reaction mixture at 55 and 70 °C are shown in Fig. 2 and Table 1. The concentration of the activated catalyst in the reaction mixture is calculated to be a hundredth to a fiftieth of the concentration of CuCl, indicating that the small portion of the polymeric ate-complexes with CuCl–KCl participates in the reaction.[17,18]

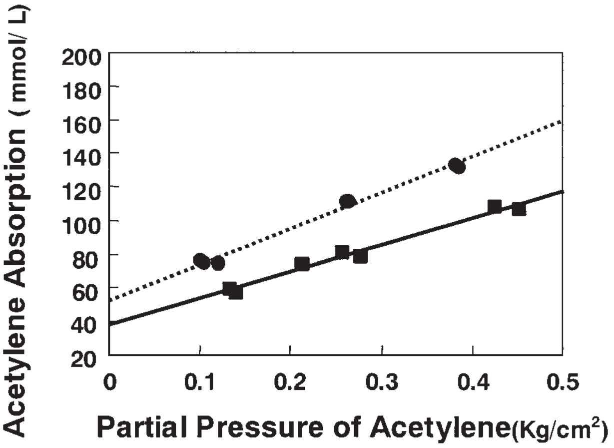

Fig. 2. The relation between the partial pressure of acetylene and the concentration of acetylene at 55 (●) and 70 (■) °C.

Table 1. Quantities of the Activation Catalyst and the Pure Acetylene Absorption

Temperature /°C	Activation catalyst /mmol•L^{-1}	Pure acetylene absorption /mmol•L^{-1}
70	38.09	163.53
67	41.70	174.70
64	45.30	185.87
61	48.91	197.05
58	50.66	209.02
55	52.42	220.99

We also measured the rate-constants of the dimerization and hydration reactions according to Eqs. 1 and 2. As shown in Fig. 3, Arrhenius plots of the reactions form a straight line: $r^2 = 0.9956$ for MVA and 0.9946 for ACH. The thermodynamic parameters obtained from the Arrhenius plots are listed in Table 2. The activation energies are 12.4 kcal•mol^{-1} for MVA, which is very close to a value already reported,[20] and 17.5 kcal•mol^{-1} for ACH. The activation Gibbs' free energies are 21.5 kcal•mol^{-1} for MVA and 27.2 kcal•mol^{-1} for ACH. The activation entropy for MVA is −33.3 cal•mol^{-1}•K^{-1}, which is almost the same as −34.2 cal•mol^{-1}•K^{-1} for ACH production. In general, the activation entropies of reactions with two molecules are about from −10 cal•mol^{-1}•K^{-1} to −25 cal•mol^{-1}•K^{-1}; for example, the activation entropy of a cyclobutane production from two ethylene molecules ($2C_2H_4 \rightarrow \square$) is −22.6 cal•mol^{-1}•K^{-1}.[23] Thus, the large absolute values of the activation entropies may be attributed to the participation of water molecules (or oxonium ion (H_3O^+) because of a very low value of the pH (<1) in the reaction system) in both reactions, because the water molecule as a reactant might limit the movement of water molecules as a solvent through a hydrogen-bond network. Furthermore, theoretical calculations on the mechanism of the Cu(I) catalysed-dimerization and hydration of acetylene to confirm the contribution of oxonium ion as a co-catalyst are currently under way. The results of the theoretical calculations will be published in the near future.

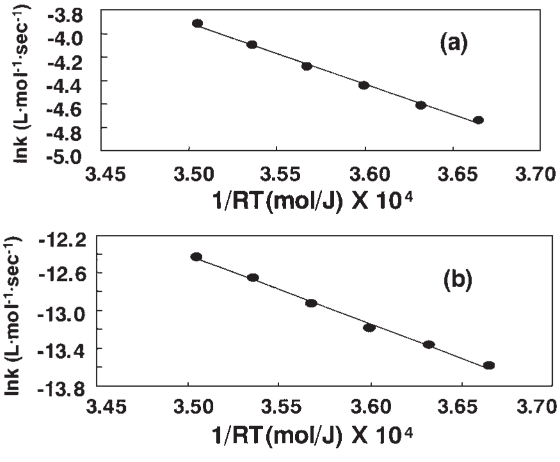

Fig. 3. Arrhenius plots of the acetylene dimerization and hydration: (a) MVA and (b) ACH.

Table 2. Thermodynamics Parameters of MVA and ACH Productions

	E_a /kcal•mol^{-1}	$\log_{10} A$ /s^{-1}	$\Delta S^\ddagger$ /cal•mol^{-1}•K^{-1}	$\Delta G^\ddagger$ /kcal•mol^{-1}
MVA	12.4 (15.5[a)])	6.17	−33.3	21.5
ACH	17.5	5.75	−34.2	27.2

E_a, A, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ are the activation energy, frequency factor, activation entropy, and Gibbs free energy, respectively. a) Ref. 20.

Conclusion

The thermodynamic parameters for the dimerization and hydration of acetylene in water with a copper(I) catalyst were determined by the stationary state kinetics using the concentration of activated catalyst measured experimentally. Although the activation Gibbs' free energy for MVA is 21.5 $\mathrm{kcal \cdot mol^{-1}}$, and is smaller than 27.2 $\mathrm{kcal \cdot mol^{-1}}$ for ACH, the activation entropy for MVA is -33.3 $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$, and almost the same as -34.2 $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$ for ACH production. The large thus-obtained absolute values of the activation entropies strongly suggest the participation of the oxonium ion in both reactions as a cocatalyst.

Experimental

Kinetics. A kinetic model of the reactions is shown in Fig. 4.[24] It is assumed that the dimerization and hydration of acetylene are second-order reactions of an activation catalyst, $[\mathrm{H \cdots Cl{-}Cu{-}C_2H}]$ formed in the reaction mixture, with acetylene and water molecules, respectively. We also assume that the formations of DVA and ADV are bimolecular reactions between the activated catalyst and MVA. The direct production of DVA and ADV from the complex of the activated catalyst and AC is not included in our model reaction, because since the activated catalyst has a d^{10} electronic structure of Cu(I), multi-ligation of acetylene molecules may be impossible. This suggestion also agrees with our results of the theoretical calculations (unpublished results). Furthermore, since the intermediate ($\mathrm{ClCu{-}C{=}C{-}C{\equiv}CH}$) may be pushed out by a large amount of acetylene,[22] the direct production of DVA and ADV from the complex of the activated catalyst and AC can be ignored. Since the reaction system reaches a steady state by 30 min after the start of acetylene introduction, the kinetics can be described based upon the stationary state. The rate constants of the dimerization (k_1) and the hydration of acetylene (k_4) are given by

$$k_1 = \frac{V_\mathrm{B} + V_\mathrm{C} + V_\mathrm{D}}{C_\mathrm{A0}(T)S(T)} \tag{1}$$

and

$$k_4 = \frac{V_\mathrm{E}}{C_\mathrm{w}S(T)}, \tag{2}$$

respectively, where $C_\mathrm{A0}(T)$ is the initial concentration of acetylene, C_w the water concentration (36.185 $\mathrm{mol \cdot L^{-1}}$) and $S(T)$ the concentration of activated catalyst at T Kelvin. V_i is an effusion rate of gas i, and is defined as

$$V_i = Z \times \frac{x_i}{100} \times \frac{1}{22.4} \times \frac{1}{3}, \tag{3}$$

where x_i is the content of gas i (%) and Z is the rate of acetylene introduction. Under the experimental condition, Z is 0.208 $\mathrm{L \cdot s^{-1}}$, which is large enough not to be a feed-controlled reaction (unpublished result). The details of the derivation of rate constants are described in the appendix.

Concentration of Acetylene. In order to obtain the stationary state concentrations of acetylene and an activated catalyst, we measured the amount of acetylene absorbed into the reaction mixture. The apparatus used in the experiment is shown in Fig. 5. An aqueous catalyst solution of 600 mL contained CuCl (5.50 $\mathrm{mol \cdot L^{-1}}$) and KCl (6.05 $\mathrm{mol \cdot L^{-1}}$), and was stirred continuously with an anchor wing at 900 rpm. First, the pressure of an acetylene tank of 12.25 L was set to P1, followed by opening valve V2 and introducing acetylene into the reaction vessel; the pressure of the acetylene tank decreased to P2. The total amount of acetylene supplied into the reaction vessel was estimated from the difference between P1 and P2. The pressure of the reaction vessel decreased from P3 to P4 just after closing valve V2. The amount of the acetylene absorbed into the reaction mixture was calculated from the P4 and the total amount of the acetylene supplied.

Flow Rate of Effusive Gases. The rate of effusive gas flow was measured by using the apparatus shown in Fig. 6. The reaction mixture was stirred by bubbling acetylene at the bottom of the reaction vessel and inducing a downward flow in the side pipe. The volume of the reaction mixture was 3 L, and the rate of acetylene supply was 0.208 $\mathrm{L \cdot s^{-1}}$. After confirming the stationary state, the composition of the effusion gas was determined by GC. The measurements were repeated three times at 3 °C intervals from 55 to 70 °C.

Appendix

Since acetylene gas is always supplied in excess, the concentration of acetylene in the reaction mixture (C_A) remains unchanged, and is defined as

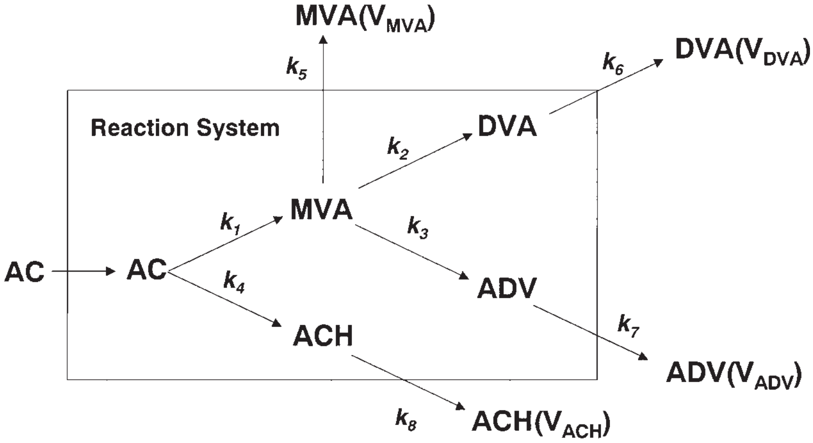

Fig. 4. A kinetic model of the reactions. AC denotes acetylene, k_1, k_2, k_3, and k_4 are the rate constants for MVA, DVA, ADV, and ACH productions, respectively, and k_5, k_6, k_7, and k_8 are the rate constants of the effusion of MVA, DVA, ADV, and ACH, respectively. V_B, V_C, V_D, and V_E are the effusion rates of MVA, DVA, ADV, and ACH, respectively.

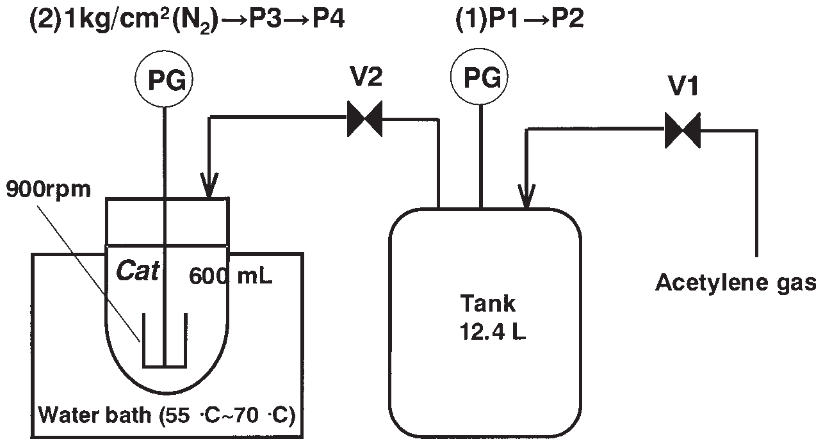

Fig. 5. A schematic flow diagram for the experiment of the acetylene absorption.

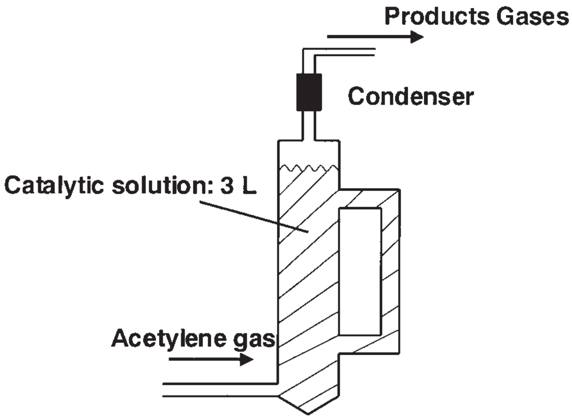

Fig. 6. A schematic diagram for the experiment of the flow rates of gases.

$$C_A = C_{A0}(T), \tag{1A}$$

where $C_{A0}(T)$ is the initial concentration of acetylene at T Kelvin. The time differentiation of the concentration of MVA (C_B) is given by

$$\frac{dC_B}{dt} = k_1 C_{A0}(T)S(T) - (k_2S(T) + k_3S(T) + k_5)C_B, \tag{2A}$$

where k_1, k_2, and k_3 are the rate constants of MVA, DVA, and ADV production, respectively, k_5 the rate constant of MVA effusion from the reaction system, and $S(T)$ is the concentration of activated catalyst at T Kelvin. From Eq. 2A the concentration of MVA leads to

$$C_B = \frac{k_1}{(k_2 + k_3)S(T) + k_5} S(T)C_{A0}(T)(1 - e^{-(k_2S(T)+k_3S(T)+k_5)t}). \tag{3A}$$

In Eq. 3A, C_B is constant at infinite time,

$$C_B = \frac{k_1}{(k_2 + k_3)S(T) + k_5} S(T)C_{A0}(T), \tag{4A}$$

corresponding to the MVA concentration under the stationary state. The time differentiation of the concentration of DVA (C_C) is given by

$$\frac{dC_C}{dt} = \frac{k_1k_2S(T)^2}{(k_2 + k_3)S(T) + k_5} \times C_{A0}(T)(1 - e^{-(k_2S(T)+k_3S(T)+k_5)t}) - k_6C_C, \tag{5A}$$

where k_6 is the rate constant of DVA effusion. From Eq. 5A the concentration of DVA leads to

$$\begin{aligned} C_C = {} & [k_1k_2S(T)^2C_{A0}(T)\lfloor\{(k_2 + k_3)S(T) + k_5\}(1 - e^{-k_o t}) \\ & - k_6\{1 - e^{-(k_2S(T)+k_3S(T)+k_5)t}\}\rfloor] \\ & /[k_6\{(k_2 + k_3)S(T) + k_5\}\{(k_2 + k_3)S(T) + k_5 - k_6\}]. \end{aligned} \tag{6A}$$

In Eq. 6A, C_C is constant at infinite time,

$$\begin{aligned} C_C &= \frac{k_1k_2C_{A0}(T)S(T)^2\{(k_2 + k_3)S(T) + k_5 - k_6\}}{k_6\{(k_2 + k_3)S(T) + k_5\}\{(k_2 + k_3)S(T) + k_5 - k_6\}} \\ &= \frac{k_1k_2C_{A0}(T)S(T)^2}{k_6\{(k_2 + k_3)S(T) + k_5\}}, \end{aligned} \tag{7A}$$

corresponding to the DVA concentration under the stationary state. The ADV concentration (C_D) at the stationary state is given by

$$C_D = \frac{k_1k_3S(T)^2C_{A0}(T)}{k_7\{(k_2 + k_3)S(T) + k_5\}}, \tag{8A}$$

where k_7 is the rate constant of ADV effusion. The time differentiation of the concentration of ACH (C_E) is given by

$$\frac{dC_E}{dt} = k_4C_wS(T) - k_8C_E, \tag{9A}$$

where C_w is the concentration of water (36.185 mol•L^{-1}), k_4 the rate constants of ACH production and k_8 the rate constant of ACH effusion. The ACH concentration at the stationary state is given by

$$C_E = \frac{k_4}{k_8} C_wS(T). \tag{10A}$$

Assuming that the effusion rates of gases are proportional to each concentration of ones, the effusion rates are defined as

$$V_B = k_5C_B, \tag{11A}$$

$$V_C = k_6C_C, \tag{12A}$$

$$V_D = k_7C_D, \tag{13A}$$

and

$$V_E = k_8C_E, \tag{14A}$$

where V_B, V_C, V_D, and V_E are the effusion rates of MVA, DVA, ADV, and ACH, respectively. From Eqs. 4A, 7A, 8A, 11A, 12A, and 13A, C_B, C_C, and C_D are related to V_B, V_C, and V_D, respectively, in the following forms:

$$C_B = \frac{k_1 S(T)}{(k_2 + k_3)S(T) + k_5} C_{A0}(T) = \frac{V_B}{k_5}, \tag{15A}$$

$$C_C = \frac{k_1 k_2 S(T)^2}{k_6\{(k_2 + k_3)S(T) + k_5\}} C_{A0}(T) = \frac{V_C}{k_6}, \tag{16A}$$

and

$$C_D = \frac{k_1 k_3 S(T)^2}{k_7\{(k_2 + k_3)S(T) + k_5\}} C_{A0}(T) = \frac{V_D}{k_7}. \tag{17A}$$

From Eqs. 15A and 16A, k_2 leads to

$$k_2 = \frac{k_5}{S(T)} \frac{V_C}{V_B}. \tag{18A}$$

From Eqs. 15A and 17A, k_3 leads to

$$k_3 = \frac{k_5}{S(T)} \frac{V_D}{V_B}. \tag{19A}$$

When Eqs. 18A and 19A are substituted in Eq. 15A, k_1 is obtained by

$$k_1 = \frac{V_B + V_C + V_D}{C_{A0}(T)S(T)}. \tag{20A}$$

Finally, from Eqs. 10A and 14A, k_4 is given by

$$k_4 = \frac{V_E}{C_w S(T)}. \tag{21A}$$

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24 Since the total amounts of the others (tetramer, pentamer, and so on) are less than 2% per acetylene consumed, the material balance is almost consistent in our experimental condition.