

Mechanistic study on dimerization of acetylene with a Nieuwland catalyst

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A mechanistic study on the Nieuwland catalysis for dimerization of acetylene is performed by detecting copper–acetylene and copper–monovinylacetylene π -complexes and also by examining the kinetics under virtually the same reaction conditions employed in the industrial process. An efficient H/D exchange occurs between acetylene and protons in the Nieuwland catalytic system. Addition of a coordinating ligand to the conventional Nieuwland catalytic system results in improvement of the catalytic activity and selectivity for the acetylene dimerization. The kinetic analysis including the kinetic deuterium isotope effect provides valuable insight into the Nieuwland catalytic mechanism of the dimerization of acetylene. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: copper complex; acetylene; Nieuwland catalyst; H/D exchange

Introduction

A Nieuwland catalyst, which is composed of CuCl and KCl or NH₄Cl in aqueous media, has long been used for acetylene dimerization on an industrial scale.^[1–7] The Nieuwland catalytic system makes it possible to dimerize acetylene to afford monovinylacetylene without formation of benzene or a linear acetylene trimer. Monovinylacetylene (MVA) is then easily converted to chloroprene, which is an important starting material for the synthetic rubber.^[8–10] The catalytic reaction is performed in aqueous solutions containing extremely high concentrations of CuCl and KCl (or NH₄Cl) under the proper pH range to inhibit formation of explosive copper acetylide and without exposure of the products to oxygen to prevent ignition of divinylacetylene (DVA) formed as a by-product. Such an aqueous Nieuwland catalytic system is environmentally favorable as compared with those with transition metal complexes normally performed in organic solvents.^[11–13] On the other hand, there has been increased interest in the addition reaction of terminal alkynes in water.^[14–16]

Despite the long history and the practical importance of the Nieuwland catalyst, there have been only a few mechanistic studies on the Nieuwland catalysis.^[17–19] Crystallographic studies of solid products recovered from Nieuwland aqueous solutions of NH₄Cl and CuCl have revealed several structures of chlorocuprates, (Cu⁺)_m(Cl[−])_n.^[20,21] The Nieuwland catalyst is known to exist as multinuclear copper(I) complexes in the solution because of high concentration and the tendency of CuCl and Cu(CCR) to aggregate via bridging of the ligands.^[20,21] However, extremely high concentrations of CuCl and KCl (or NH₄Cl) under the proper pH range required for the Nieuwland catalytic system has precluded the detailed mechanistic study. The copper–acetylene complex, Cu(C₂H₂)⁺, that has been detected in the gas phase, may be a potential intermediate for the catalytic dimerization of acetylene,^[22–25] as indicated by the quantum chemical study of the structure and bonding of copper–acetylene complexes.^[26–29] A number of copper alkynyl complexes have also been reported as metal-based functional materials.^[30–34]

However, a copper–acetylene complex intermediate has yet to be detected in a Nieuwland catalytic system.

We report herein the first mechanistic study on the Nieuwland catalysis for dimerization of acetylene including direct detection of the copper–acetylene and copper–monovinylacetylene π -complexes under virtually the same reaction conditions employed in the industrial process. We have found efficient H/D exchange between acetylene and proton in the Nieuwland catalytic system. The effect of an additional ligand on the conventional Nieuwland catalytic system has also been examined, leading to improvement of the catalytic activity and selectivity. The kinetic analysis, including the kinetic deuterium isotope effect, provides valuable insight into the catalytic mechanism of the dimerization of acetylene.

Experimental

Materials and reagents

CuCl was purchased from Nihon Kagaku Sangyo and KCl was purchased from Mitsui Bussan in industrial grade. D₂O (99.9 atom% D), acetylene-d₂ (99 atom% D) and acetylene-¹³C₂ (99 atom% ¹³C) were obtained from Isotec. Acetylene was synthesized by Denki Kagaku Kogyo Co. Ltd. MVA was obtained by acetylene dimerization with a Nieuwland catalyst. DVA was a minor product of acetylene dimerization, and separated from other products by extraction. They were all used without further purification.

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Preparation of a Nieuwland catalyst solution

A mixture of CuCl (34.65 g, 0.350 mol) and KCl (24.80 g, 0.333 mol) was dissolved in 29.9 mL of distilled water (or D₂O) at 343 K under nitrogen stream and stirred for 30 min. An aqueous solution of [CuCl] = 7.0 M of Nieuwland catalyst was obtained (50 mL).

Time-course of products in the gas phase

The catalyst solution (15 mL) was added into a three-necked flask and acetylene gas (the flow rate, 20 mL/min) was passed into the solution for 15 min. As soon as acetylene supply was stopped, the gas phase was substituted to nitrogen and the flask was sealed. The gas phase was analyzed every 30 min by GC (Shimadzu GC-14A equipped with a thermal conductivity detector and a DEGS Chamelite FK chromatography column).

Preparation of ¹H-NMR samples passing acetylene and time-course of products in the catalyst solution

The catalyst was prepared by H₂O or D₂O. The solution was quickly added into a NMR tube at 323 K. Acetylene (the flow rate, 360 mL/h) was passed into the solution for 3 min. After babbling acetylene, a capillary tube was inserted into the NMR tube. The capillary tube contained 1000 ppm of TSP [3-(trimethylsilyl)propanesulfonic acid, sodium salt] as an internal standard and D₂O as a solvent. The number of scans was 64 times for 7 min, and the average time of each scans was defined as a reaction time. The prepared samples were measured at every 15 min to keep the intended temperature. After 2 h, the interval was changed to 30 min.

Preparation of ¹³C-NMR samples passing acetylene and time-course of products in the catalyst solution

The catalyst solution was quickly added into an NMR tube of 8 mm diameter at 323 K. ¹³C-labeled acetylene (C₂H₂ : N₂ = 64 : 36, flow rate, 730 mL/h) was passed into the solution for 8.6 min. The acetylene volume was determined on the basis of the acetylene/catalyst ratios as the same as ¹H-NMR measurements. After babbling acetylene, the NMR tube was inserted into another NMR tube of 10 mm diameter. The 10 mm NMR tube contained 1000 ppm of DMSO as an internal standard and D₂O as a solvent. The number of scans was 20,000 times for 25 min, and the average time of each scan was defined as a reaction time. The prepared samples were measured every 30 min to keep the intended temperature.

Measurements of NMR spectra

¹H-NMR spectra were recorded at 323 K on Jeol GSX-400 spectrometer, and chemical shifts were measured at $\delta = 0$ relative to internal TSP. ¹³C-NMR spectra were recorded at 323 K on a Jeol GSX-400 spectrometer, and chemical shifts were measured at $\delta = 50.1$ ppm of methanol as reference material.

GC-MS measurements of products in the gas phase passing acetylene

The catalyst solution (15 mL) was added into a three-necked flask and acetylene or MVA (flow rate, 60 mL/min) was passed into the solution for 5 min. As soon as acetylene supply was stopped, the gas phase was substituted to nitrogen and the flask was sealed. The gas phase was analyzed every 1 h by GC-MS (Shimadzu GCMS-QP5000 equipped with a DB-1 chromatography column).

Results and Discussion

The reactant (acetylene) and products (MVA and DVA) were detected by GC-MS at 120 min after the reaction was started as shown in Fig. 1 (see Experimental for the procedure).

Figure 1(a) shows a GC-MS spectrum of the product mixture in the gas phase at 120 min after starting the reaction of HC \equiv CH in H₂O with a Nieuwland catalyst (although there is the acetylene–acetylene interaction in aggregation in the solid phase, acetylene exists as the monomer in the gas phase; see Shuler and Dykstra^[35]). The MS signal at $m/e = 26$ due to HC \equiv CH disappears completely, accompanied by appearance of MS peaks due to MVA ($m/e = 52$) and DVA ($m/e = 78$).

The time course of the products released to the gas phase was monitored by GC at 323 K. Under the present experimental conditions, the catalyst solution remains homogeneous. The reactant and products in the gas phase were analyzed by GC. The amount of DVA formed in the gas phase increased, accompanied by a decrease in that of MVA and acetylene. Thus, the reaction proceeds in a stepwise manner: the dimerization of acetylene to give MVA and the further reaction of MVA with acetylene to give DVA.

When H₂O is replaced by D₂O under otherwise the same experimental conditions, the reactant peak due to acetylene still remains [Fig. 1(b)]. However, the observed mass number in Fig. 1(b) indicates that HC \equiv CH is converted to DC \equiv CD ($m/e = 28$)

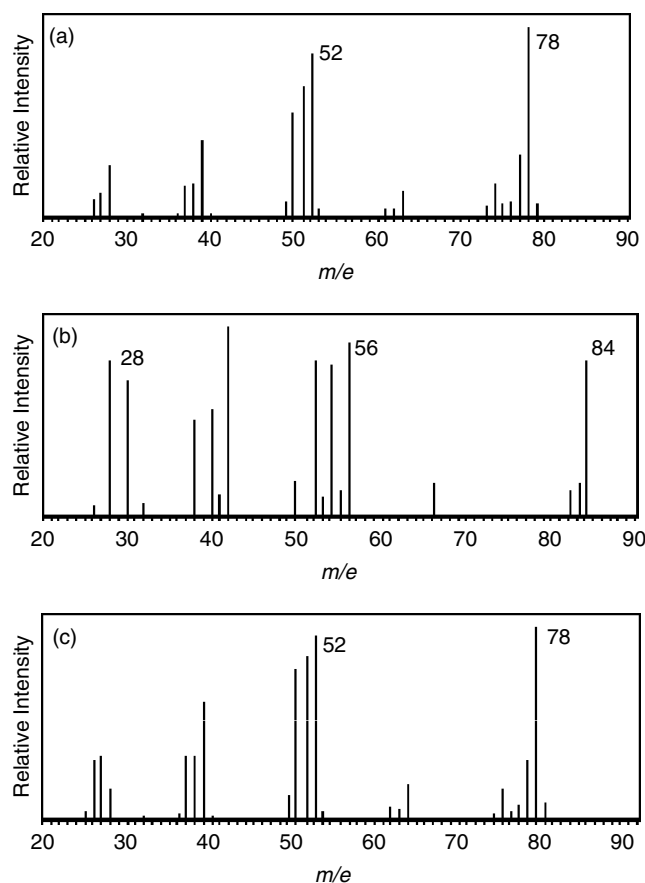


Figure 1. MS spectra of the product mixture in the gas phase at 120 min after introduction of (a) C₂H₂ into an H₂O solution, (b) C₂H₂ into a D₂O solution and (c) C₂D₂ into an H₂O solution in the presence of a Nieuwland catalyst.

in D_2O . In addition, MVA and DVA are also deuterized to give $CD_2=C(D)C\equiv CD$ ($m/e = 56$) and $CD_2=C(D)C\equiv C(D)C\equiv CD_2$ ($m/e = 84$), respectively. Thus, a Nieuwland catalyst provides a convenient way to obtain the deuterized monovinylacetylene and divinylacetylene.

When $HC\equiv CH$ is replaced by $DC\equiv CD$ and the reaction is carried out in H_2O , virtually the same result is obtained as shown in Fig. 1(c) as the reaction of $HC\equiv CH$ in H_2O [Fig. 1(a)]. These results clearly indicate that the H/D exchange between acetylene and water occurs efficiently with a Nieuwland catalyst.

The occurrence of H/D exchange between acetylene and proton in water suggests that deprotonation or dedeuteriation of acetylene is involved in the Nieuwland catalysis to produce a σ -complex of deprotonated or dedeuterinated acetylene with copper(I) species, as shown in Fig. 2, where the catalytically active species is shown in parentheses: $[Cu-C\equiv CH(orD)]$. In D_2O the proton or deutron source is only D^+ and thereby $HC\equiv CH$ is converted to $HC\equiv CD$ [Fig. 2(a)] and then to $DC\equiv CD$ [Fig. 2(b)] via a σ -complex of dedeuterinated acetylene with copper(I) species. Similarly when the reaction is started from $DC\equiv CD$ in H_2O , $DC\equiv CD$ is converted to $HC\equiv CD$ and then to $HC\equiv CH$.

1H NMR spectra of the reaction mixture were measured to detect the reaction intermediates during the catalytic dimerization of acetylene (see Experimental). After the NMR tube was sealed, the reaction was monitored at 323 K. At 15 min, the large singlet signal is observed at $\delta = 5.45$ ppm [Fig. 3(a)] and there was no signal due to uncomplexed acetylene ($\delta = 2.35$ ppm). The signal of 5.45 ppm is assigned to a π -complex of acetylene with the Nieuwland catalyst, because a similar lower field shift of acetylene peak has been reported for the π -complex formation of acetylene with $CuCl$ in HCl .^[36] The chemical shifts of acetylene protons were also observed at 5.14 and 5.59 ppm in the report on 1H NMR spectra of two copper(I) acetylene complexes, $[Cu\{NH(py)_2\}(C_2H_2)](BF_4)$ (py = pyridine) and $[Cu(phen)-(C_2H_2)](ClO_4)$ ($phen$ = 1,10-phenanthroline), as shown in Table 1.^[37,38]

As the copper(I)-acetylene π -complex disappears, the 1H NMR signals due to the copper(I)-DVA complex increase, accompanied by a decrease in those due to the copper(I)-MVA complex [Fig. 3(b)]. We have measured 1H NMR spectra of the authentic π -complexes of MVA and DVA in the catalyst solution without acetylene at 323 K, which are significantly changed from those without the catalyst in H_2O , in order to assign the 1H NMR spectra

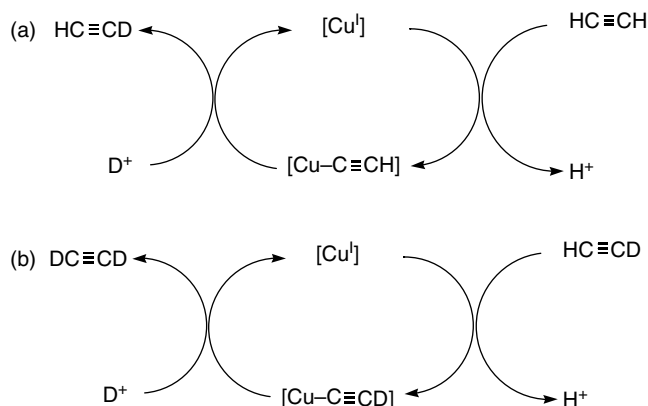


Figure 2. A plausible mechanism of H/D exchange between acetylene and proton in the presence of a Nieuwland catalyst via formation of a σ -complex of deprotonated acetylene with Cu^I species; formation of (a) $HC\equiv CD$ and (b) $DC\equiv CD$.

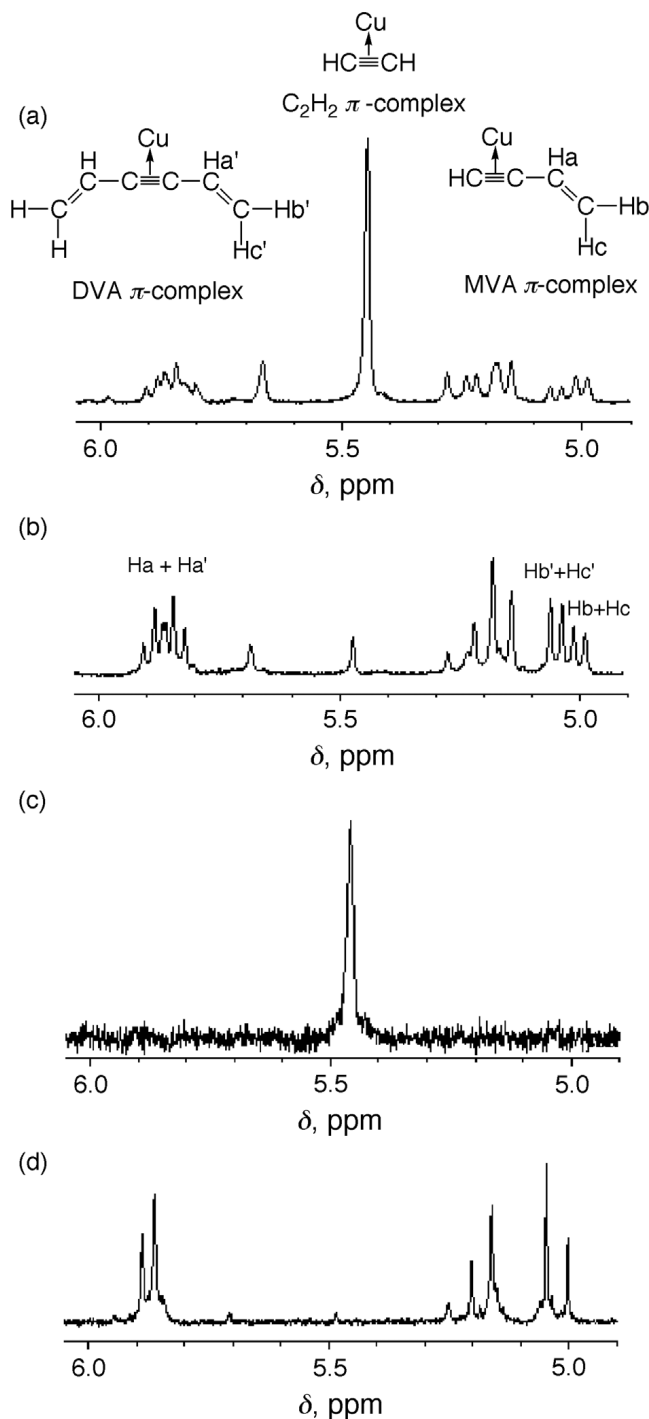


Figure 3. 1H NMR spectra of the catalyst solution containing $CuCl$, KCl and H_2O ($[CuCl] = 7.0$ M) at 323 K taken after passing acetylene (flow rate 360 mL/h) for 3 min at (a) 15 min and (b) 360 min. 1H NMR spectra of the catalyst solution containing $CuCl$, KCl and D_2O ($[CuCl] = 7.0$ M) at 323 K taken after passing acetylene (flow rate 360 mL/h) for 3 min at (c) 15 min and (d) 360 min.

of the π -complexes. The complete assignment was rather difficult because the olefinic moieties as well as the alkynyl ones might be coordinated to copper. In addition, their 1H NMR signals are largely overlapped. However, the doublet signal at 5.00 ppm ($J = 8.2$ Hz) due to the MVA complex is clearly distinguished from the signal at 5.05 ppm ($J = 8.2$ Hz) due to the DVA complex. The chemical

shifts of alkene protons in the MVA complex were compared with those in the Cu(I)–styrene complex, [Cu(bipy)(CH₂CHPh)(ClO₄)] (bipy = 2,2'-bipyridine) in Table 2.^[39] The chemical shift for the proton of trans position to phenyl group is at 5.03 ppm (styrene coordinated to copper) and 5.22 ppm (free styrene) and this proton exhibits in the most upfield in the three alkenyl protons.

When H₂O is replaced by D₂O, the ¹H NMR signal due to the copper(I)–acetylene π -complex [Fig. 3(b)] under otherwise the same experimental conditions becomes much smaller as compared with that in H₂O [Fig. 3(c)]. This is consistent with the occurrence of H/D exchange between acetylene and proton in D₂O (Fig. 2). The ¹H NMR signals due to the MVA and DVA π -

complexes also become much smaller and simpler because of the partial dueterization [Fig. 3(d)].

We also measured ¹³C NMR spectra of the Nieuwland catalyst aqueous solution using acetylene-¹³C₂. After the NMR tube was sealed, the reaction was monitored at 323 K. The MVA polymerization takes place in the catalyst by overnight ¹³C NMR measurements. *It should be cautioned that long-time measurements of DVA in the catalyst at 323 K may cause ignition by heating.* The broad signal is observed at δ = 76.5 ppm at 30 min, which is assigned to the π -complex of acetylene with the Nieuwland catalyst [Fig. 4(a)]. There was no signal due to uncomplexed acetylene (δ = 73.4 ppm) in D₂O, and the chemical shift change between free and complexed acetylene was 3.1 ppm. This is comparable to those observed in the ¹³C NMR spectra of alkyne–copper complexes, which were in the range 5.0–10.0 ppm,^[40] and also that of the reported acetylene–Cu(I) complex in an HCl aqueous solution, which was 1.1 ppm (Table 3).^[36]

To assign MVA and DVA π -complexes with the catalyst, ¹³C NMR chemical shifts were also compared with other alkyne–copper and alkene–copper complexes (Table 3). The ¹³C NMR signals of ethylene–copper(I) complexes exhibited a 30–40 ppm upfield shift as compared with free ethylene (123.5 ppm).^[41,42] The chemical shifts of terminal alkynes were 80–90 ppm. The ¹³C NMR chemical shifts of alkyne carbon of 3-hexyne and diphenylacetylene coordinated to Cu(hfac) complex, whose structures were similar to DVA, were observed at 87.9 and 95.1 ppm.^[40] As the acetylene π -complex disappeared, the ¹³C NMR signals at 89.5 and 98.3 ppm appeared [Fig. 4(b)]. The peaks at 89.5 and 98.3 ppm were assigned to the carbons of copper(I) π -complexes of MVA and DVA, respectively. The peak at 89.5 ppm was assigned to the terminal alkynyl carbon, because the peak exhibited more down-field shift as compared with the peak from the internal alkynyl carbon of the DVA complex. However, further detailed assignment of alkyne and alkene carbons of the copper(I) π -complexes has yet to be made because the olefinic moieties as well as the alkynyl ones might be coordinated to copper.

The time course of the acetylene dimerization reaction in the catalyst solution was monitored by ¹H NMR (see Experimental). The result is shown in Fig. 5(a), indicating that the acetylene π -complex

Table 1. Selected ¹H NMR chemical shifts of acetylene in ppm

Compound ^a	CH \equiv CH	Reference
Acetylene ^b	2.35	This work
[Cu](CH \equiv CH) ^c	5.45	This work
[Cu{NH(py) ₂ }(C ₂ H ₂)(BF ₄) ^d	5.14	[37]
[Cu(phen)(C ₂ H ₂)(ClO ₄) ^d	5.59	[38]

^a [Cu] represents the active site in the Nieuwland catalyst.
^b In D₂O.
^c A Nieuwland catalyst aqueous solution.
^d In (CD₃)₂CO.

Table 2. Selected ¹H NMR chemical shifts of alkene in ppm

Compound ^a	R(H)C=CH ₂ ^d	Reference
[Cu](MVA) ^b	5.00 ^e	This work
[Cu](DVA) ^b	5.05 ^e	This work
CH ₂ =CHPh ^c	5.22	[39]
[Cu(bipy)(CH ₂ =CHPh)(ClO ₄) ^c	5.03	[39]

^a [Cu] represents the active site in the Nieuwland catalyst.
^b A Nieuwland catalyst aqueous solution.
^c In CD₃OD.
^d Proton *trans* to R group.
^e *J* = 8.2 Hz.

Table 3. Selected ¹³C NMR chemical shifts of alkyne and alkene in ppm

Compound ^a	RC \equiv CR'	R-CH=CH ₂	Reference
[Cu](CH \equiv CH) ^b	76.5		f
[Cu](MVA) ^b	89.5	93.7	f
[Cu](DVA) ^b	93.7	98.3	f
Cu(hfac)(3-hexyne) ^c	87.9		[40]
Cu(hfac)(diphenylacetylene) ^c	95.1		[40]
[Cu(phen)(HC \equiv CPh)(ClO ₄) ^d	79.7		[38]
[HB(3,5-(CF ₃) ₂ Pz) ₃]Cu(C ₂ H ₄) ^e		89.5	[41]
[t-Bu ₂ P(Me ₃ SiN) ₂]Cu(C ₂ H ₄) ^e		73.0	[42]

^a [Cu] represents the active site of the Nieuwland catalyst.

^b A Nieuwland catalyst aqueous solution.

^c In CDCl₃.

^d In (CD₃)₂CO.

^e In C₆D₆.

^f This work.

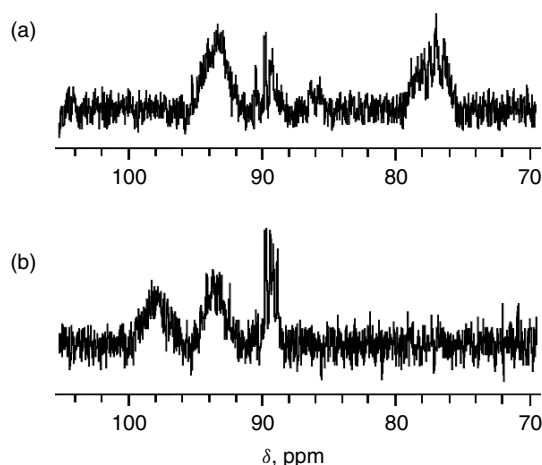


Figure 4. ¹³C NMR spectra of MVA and DVA complexes with a Nieuwland catalyst in H₂O at 323 K after passing acetylene-¹³C₂ (C₂H₂ : N₂ = 64 : 36, flow rate 730 mL/h) for 8.6 min at (a) 15 min and (b) 300 min.

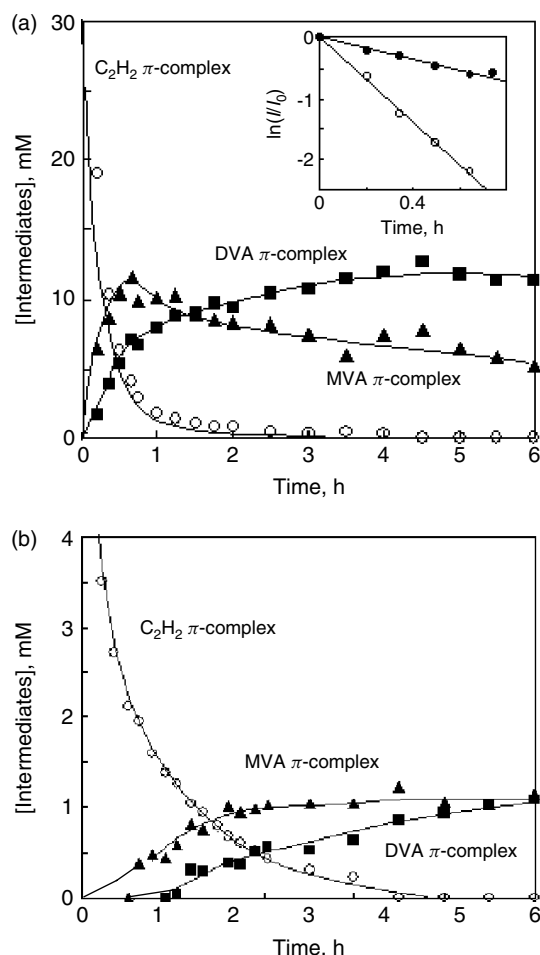


Figure 5. (a) Time profiles of concentrations of intermediates in the catalyst solution ($[\text{CuCl}] = 7.0 \text{ M}$) at 323 K ; C_2H_2 π -complex (\circ), MVA π -complex (\blacktriangle) and DVA π -complex (\blacksquare). Inset: first-order plot of the ratio of ^1H NMR signal intensity due to the Cu–acetylene π -complex to the initial intensity (I/I_0) in H_2O (\circ) and D_2O (\bullet). (b) Time profiles in D_2O .

with the Nieuwland catalyst is converted to the MVA π -complex and then to the DVA π -complex by the reaction between the acetylene π -complex and the MVA π -complex. The decay of the acetylene π -complex in H_2O obeys first-order kinetics as shown in the inset of Fig. 5(a) (open circles).

When H_2O was replaced by D_2O , the observed concentrations of the acetylene, MVA and DVA π -complexes by ^1H NMR became smaller due to the H/D exchange [Fig. 5(b)] under otherwise the same experimental conditions. The first-order decay rate in the D_2O [closed circles in inset of Fig. 5(a)] was 3.9 times smaller than that in H_2O . This is also consistent with the slower consumption of acetylene measured in the gas phase for the reaction in D_2O as compared with that in H_2O . The kinetic deuterium isotope effect together with the observation of the first-order kinetics for the decay of the copper(II)–acetylene π -complex suggest that the deprotonation or dedeuteriation from the π -complex is involved in the rate-determining step to give the σ -complex that reacts with the acetylene π -complex rapidly to yield the copper(II)–MVA π -complex, as shown in Fig. 6. This may be the reason why the σ -complex is not observed during the reaction. It should be noted, however, that the H/D exchange of acetylene with water occurs much faster than

the dimerization of acetylene. The copper(II)–MVA π -complex further reacts with the acetylene π -complex via the MVA σ -complex to produce the copper(II)–DVA π -complex. The MVA and DVA π -complexes are in equilibrium with MVA and DVA in the gas phase, respectively (Fig. 6). Thus, in the actual process, acetylene should be introduced into the catalyst solution jointly and simultaneously with an inert organic solvent extractant and stripping agent for the resulting MVA, the solvent being in vapor form and being continuously passed through the catalyst solution so as to continually strip off MVA to avoid formation of DVA.

Since the copper(II)–acetylene π -complex is involved in a Nieuwland catalyst, the mechanistic scheme for the deuteration of acetylene in Fig. 2 should be modified to that shown in Fig. 7.

According to the proposed mechanism, the deprotonation of the copper(II)–acetylene π -complex is involved in the catalytic cycle, which may be accelerated by addition of a base to the

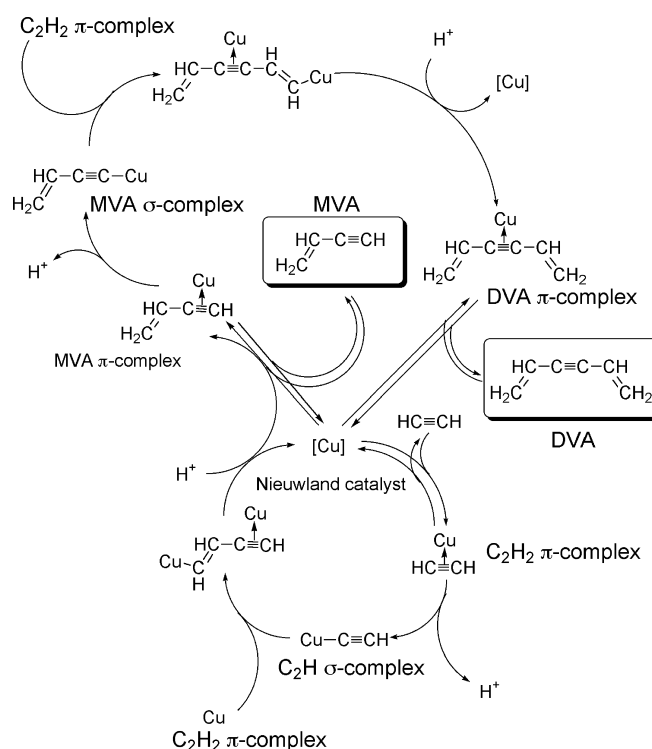


Figure 6. A proposed mechanism for the dimerization of acetylene with a Nieuwland catalyst.

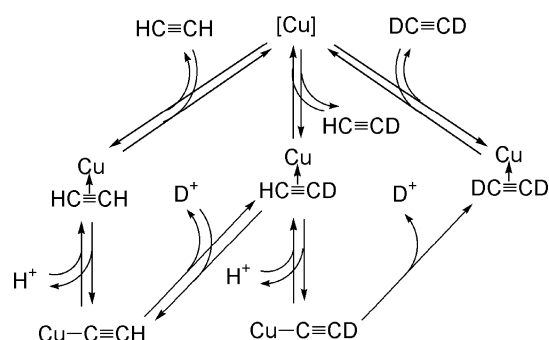


Figure 7. A proposed mechanism for the deuteration of acetylene with a Nieuwland catalyst via copper(II)–acetylene π - and σ -complexes.

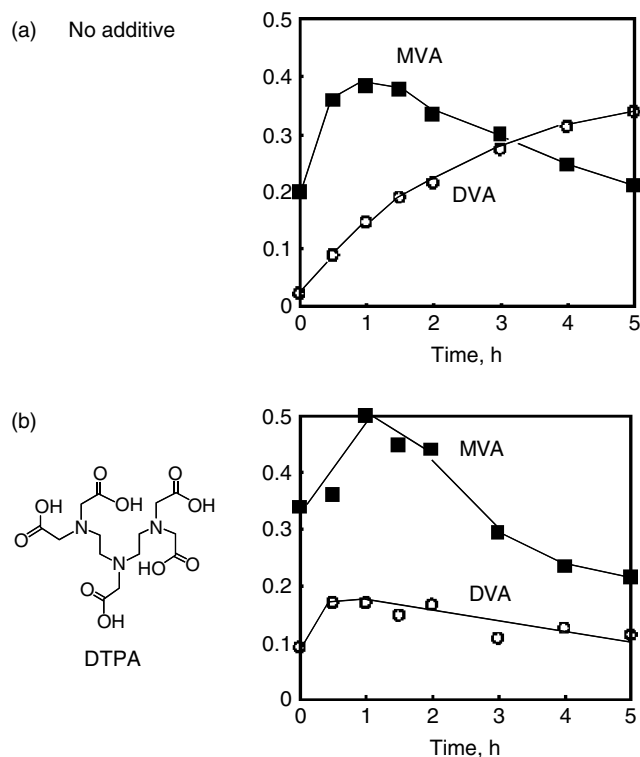


Figure 8. (a) Time profiles of formation of products [MVA (■)] and DVA (○)] detected in the gas phase in the reaction of acetylene with a Nieuwland catalyst ($[\text{CuCl}] = 7.0 \text{ M}$) (a) in the absence of DTPA and (b) in the presence of DTPA (0.20 M) at 323 K.

catalytic solution. The effect of a series of amino carboxylic ligands such as EDTA and triethylenetetraaminehexaacetic acid has been reported.^[43] However, there was no catalytic effect on the Nieuwland catalysis.^[43] We have also examined the effects of various bases such as amines, pyridine and bipyridines on the reactivity of the Nieuwland catalyst for the acetylene dimerization. In most cases, addition of bases results in formation of precipitates.

When diethylenetriaminepentaacetic acid (DTPA) was employed as an additive, the Nieuwland catalyst remained as a homogeneous solution without forming precipitates. The maximum yield of MVA became higher and the product ratio of MVA to DVA was improved in the presence of DTPA [Fig. 8(b)] as compared with that in its absence at longer reaction time [Fig. 8(a)]. Although the mechanism of the effect of DTPA on the Nieuwland catalytic system has yet to be further clarified, the coordination of DTPA to the copper(I) active species may affect the stability of the copper(I)–MVA and copper(I)–DVA complexes.

In conclusion, the dimerization of acetylene with the Nieuwland catalyst in an aqueous solution proceeds via the deprotonation of the copper(I)–acetylene π -complex to afford the σ -complex with the catalyst. In order to optimize the yield of MVA in the gas phase, it is of primary importance to eliminate MVA in the gas phase to avoid the further reaction of the copper(I)–MVA π -complex with the acetylene π -complex, which leads to formation of a byproduct, DVA. The activity and the selectivity to obtain the desired product (MVA) with the Nieuwland catalyst was improved by addition of DTPA.

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