# Deuteration and Dimerization of Acetylene with a Nieuwland Catalyst in Deuterium Oxide

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Efficient deuteration and dimerization of acetylene have been readily attained in deuterium oxide with a Nieuwland catalyst which is practically used for dimerization of acetylene.

Deuterated alkynes and alkenes are an important class of compounds, which have frequently been utilized for biological and physicochemical research, and the elucidation of reaction mechanisms. There have been a number of reports on the development of the reduction of alkynes into 1,2-deuterioalkenes with deuterium oxide ($D_2O$), which is undoubtedly the most inexpensive and easy to handle deuterium source.[1–5] With regard to acetylene, the deuterized compound DC≡CD is obtained by the reaction of calcium carbide with $D_2O$.[6] However, there has been no report on partial deuteration of acetylene with $D_2O$ to afford HC≡CD rather than fully deuterized compound DC≡CD.[7]

We report herein partial and full deuteration of acetylene and monovinylacetylene using $D_2O$ with a Nieuwland catalyst, which is composed of CuCl and KCl or $NH_4Cl$. The Nieuwland catalyst has long been used as the representative catalyst for acetylene dimerization on an industrial scale.[8–12] The catalytic reaction is carried out in aqueous solutions containing high concentrations of the $Cu^+$ and $K^+$ (or $NH_4{}^+$). Such an aqueous reaction is environmentally more benign than a number of synthetic organic reactions with transition metal complexes used for dimerization of monosubstituted acetylenes in organic solvents.[13]

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 $D_2O$) at 343 K under nitrogen stream and stirred for 30 min. An aqueous solution of $[\mathrm{CuCl}] = 7.0\,\mathrm{M}$ of the Nieuwland catalyst was obtained (50 mL). 150 mL of the catalyst solution added into the three necked flask passed acetylene (the flow rate, 0.1 L/min.) 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-MS (a Shimadzu GCMS-QP 5000 equipped with a DS-1 chromatography column).

Figure 1a shows a GC-MS spectrum of HC≡CH at $m/z = 26$ detected in the gas phase of an $H_2O$ solution of acetylene/Nieuwland catalyst. When $H_2O$ is replaced by $D_2O$, however, an H/D exchange of acetylene with $D_2O$ occurs to afford HC≡CD ($m/z = 27$) and DC≡CD ($m/z = 28$) as shown in Figure 1b. When HC≡CH is replaced by DC≡CD in an $H_2O$ solution of acetylene/Nieuwland catalyst, DC≡CD is converted to HC≡CD and HC≡CH (Figure 1c). These results clearly indicate that the Nieuwland catalyst is responsible for the H/D exchange between acetylene and water.[14]

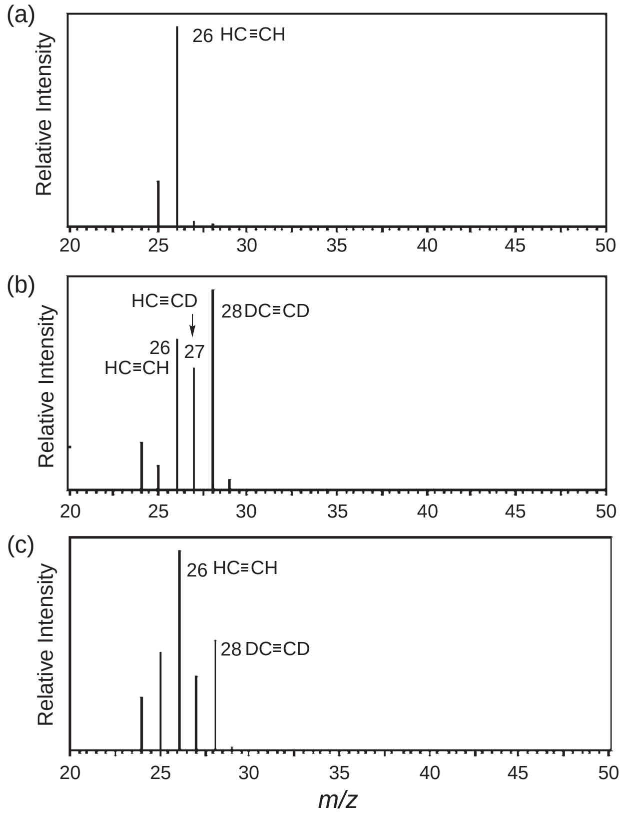
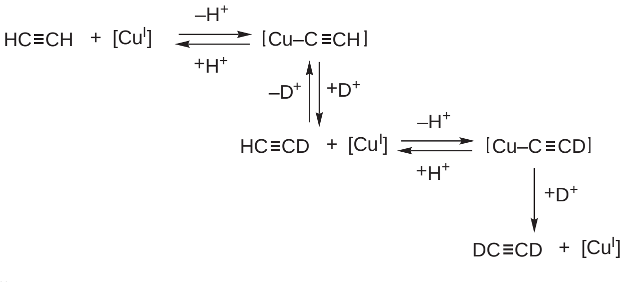


**Figure 1.** MS spectra of acetylene detected in the gas phase after introduction of (a) $C_2H_2$ into an $H_2O$ solution, (b) $C_2H_2$ into a $D_2O$ solution, and (c) $C_2D_2$ into an $H_2O$ solution in the presence of a Nieuwland catalyst.



**Scheme 1.** A plausible mechanism of H/D exchange between acetylene and proton in the presence of a Nieuwland catalyst via formation of a $\sigma$-complex of deprotonated acetylene with $Cu^I$ species.

The occurrence of H/D exchange between acetylene and proton in water suggests that deprotonation of acetylene is involved in the Nieuwland catalysis to produce a $\sigma$-complex of deprotonated acetylene with $Cu^I$ species that is in equilibrium with acetylene as shown in Scheme 1.[15] In $D_2O$ HC≡CH is converted to HC≡CD and then to DC≡CD via a $\sigma$-complex of deprotonat-

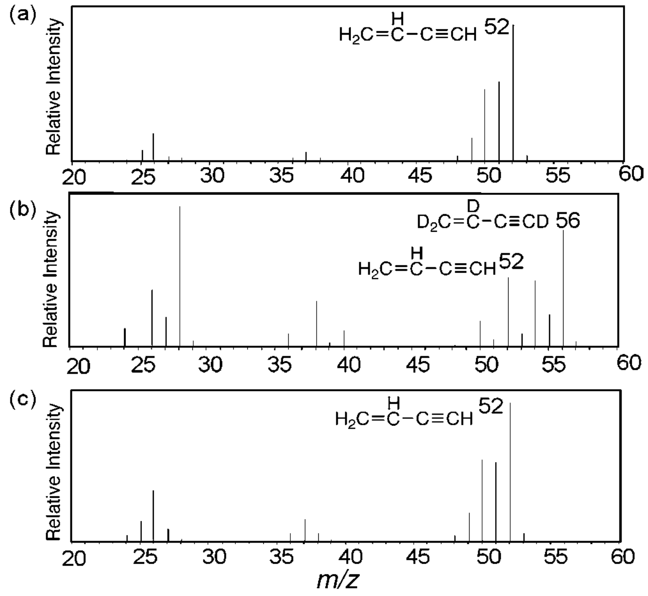


**Figure 2.** MS spectra of monovinylacetylene detected in the gas phase at 60 min after introduction of (a) $C_2H_2$ into an $H_2O$ solution, (b) $C_2H_2$ into a $D_2O$ solution, and (c) $C_2D_2$ into an $H_2O$ solution in the presence of a Nieuwland catalyst.

ed acetylene with $Cu^I$ species in Scheme 1 where the catalytically active species is shown in the parenthesis: [Cu–C≡CH(orD)]. Similarly when the reaction is started from DC≡CD in $H_2O$, DC≡CD is converted to HC≡CD and then to HC≡CH.

At 60 min after introduction of acetylene into an $H_2O$ solution of the Nieuwland catalyst, the dimerization of acetylene proceeds to afford monovinylacetylene ($CH_2$=CHC≡CH: $m/z = 52$) as shown in Figure 2a. In $D_2O$, deuterized monovinylacetylene ($CD_2$=CDC≡CD: $m/z = 56$) was produced under otherwise the same conditions (Figure 2b).[16] When the dimerization of DC≡CD was carried out in an $H_2O$ solution of the Nieuwland catalyst, $CH_2$=CHC≡CH was produced without formation of deuterized monovinylacetylene (Figure 2c).

At prolonged reaction time, the reaction of HC≡CH in $D_2O$ with the Nieuwland catalyst affords the fully deuterized monovinylacetylene and divinylacetylene. Thus, the Nieuwland catalyst provides a convenient way to obtain the fully deuterized monovinylacetylene and divinylacetylene.

It should be noted that a significant kinetic deuterium isotope effect is observed because the dimerization rate of acetylene is slowed down when HC≡CH in $H_2O$ is replaced by HC≡CH in $D_2O$ as shown in Figure 2b where DC≡CD ($m/e = 28$) still remains in contrast with the result in Figure 2a. The slower dimerization rate of HC≡CH in $D_2O$ than that of HC≡CH in $H_2O$ was confirmed by the time profile of the formation rate of the products in the gas phase. Such a kinetic deuterium effect suggests that the deprotonation of acetylene to form the $\sigma$-complex of deprotonated acetylene with $Cu^I$ species in the Nieuwland catalyst may be involved in the catalytic cycle. However, the detailed mechanisms of the catalytic dimerization of acetylene has yet to be clarified by taking into account the fact that the deuteration rate is much faster than the dimerization rate (see Figure 1).

In conclusion, we have demonstrated that partial and full deuteration of acetylene as well as deuteration of monovinylacetylene and divinylacetylene is readily achieved using a Nieuwland catalyst in $D_2O$. Such an efficient H/D exchange of acetylene with proton in water also provides valuable insight into the mechanism of the Nieuwland catalysis for dimerization of acetylene.

This work was partially supported by Grants-in-Aid (No. 19205019) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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