Table 1. Selected O-O Distances [Å] and Angles [deg] for [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme

O(7)···O(9)	3.56*	O(8)···O(9)	2.71
O(7)···O(10)	2.80*	O(8)···O(10)	3.16
O(7)···O(11)	3.16*	O(8)···O(11)	2.87
O(7)···O(12)	2.77*	O(8)···O(12)	3.71
O(10)*···O(7)···O(12)*	104.6	O(9)···O(8)···O(11)	101.7

*symmetry operation: x, 0.5-y, −0.5+z.

triglyme is unprecedented; the hydrogen bonding interaction between water molecules and the oxygen atoms of the triglyme ligand results in the one-dimensional chain. It will be interesting to understand the role of the outer-sphere polyether ligand for CVD precursors during vaporization. Further studies on the role of triglyme ligand during vaporization and on the vapor phase structure are in progress in our laboratory.

Acknowledgment. Prof. J. Ko at Korea University was appreciated for generous loans of chemicals.

Supporting Information Available. Experimental details of X-ray crystal structure determination, crystallographic tables, listing of atomic coordinates, thermal parameters, and bond distances and angles (19 pages).

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6. Crystal data for [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme; monoclinic P2$_1$/c, a=12.559(3), b=19.111(6), c=16.789(6) Å, β=110.59(4)°, V=3772(2) Å^3. The structure was solved by a heavy atom method and refined to R_1=0.047 and wR_2=0.121 against 2732 observed [I>2σ(I)] reflections.
7. Abbreviations used in this paper include: Hhfa, hexafluoroacetylacetone; hfa, anion of Hhfa; diglyme, bis(2-methoxyethyl) ether; triglyme, triethylene glycol dimethyl ether; tetraglyme, tetraethylene glycol dimethyl ether; tmhd, 2,2,6,6-tetramethylheptane-3,5-dione.
8. To a suspension of Ho_2O_3 (1.00 g, 2.65 mmol) in toluene (150 mL) were added Hhfa (2.24 mL, 15.88 mmol) and triglyme (0.95 mL, 5.29 mmol). The resulting mixture was refluxed for 40 h. After cooling the mixture was filtered and the resulting yellow solution was removed in vacuo to yield pale yellow powders. Slow evaporization of benzene solution gave pale yellow crystals suitable for X-ray crystallography. Yield: 52%. IR (KBr, cm^{-1}): 3400 (m), 2980 (m), 1655 (s), 1559 (m), 1530 (m), 1505 (s), 1255 (s), 1205 (s), 1149 (s), 1100 (s), 1020 (m), 800 (s), 655 (s), 590 (m).
9. Experiment was performed on a SETARAM TGA-92 instrument, which simultaneously carried out thermogravimetry (TGA) and differential thermal analysis (DTA). The measurement was performed in alumina crucibles under an atmosphere of flowing dry nitrogen, using heating rates of 5 °C/min. from ambient temperature up to 500 °C.
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A Mechanistic Study on Nucleophilic Additions of Amines to 3-Butyn-2-one and Formation of 3-Methylpyrazole

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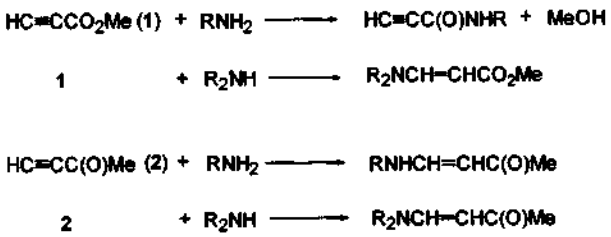
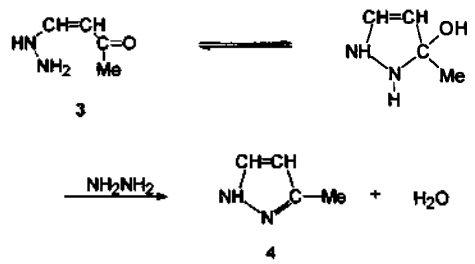
Nucleophilic additions to triple bonds have been intensively studied due to the diversity of synthetic interests.[1-4] One of the most investigated mechanism is addition mechanism of amines to activated acetylenes.[5,6] However, this mechanism has not been fully understood. Our recent study has revealed that the reactions of methyl propiolate (HC≡

CCO_2Me, **1**) with primary amines yielded mostly nucleophilic substitution products, amides from the attack at carbonyl carbon of the ester moeity, while the corresponding reactions with secondary alicyclic amines produced only addition products, enamines (Scheme 1).[7] Interestingly, the enamines formed in aprotic solvents such as diethyl ether and dioxane were found to be only trans-isomers which equilibrated with their cis-isomers in aqueous medium.[7]

We have now chosen 3-butyn-2-one ($HC\equiv CC(O)Me$, **2**) as a substrate and performed kinetic studies with glycylglycine, hydrazine and morpholine. The reaction of **2** with these amines produced the corresponding addition product, enamines (Scheme 1). However, the enamine (**3**) formed from the reaction of **2** with hydrazine proceeded further reaction to yield 3-methylpyrazole (**4**) *via* intramolecular nucleophilic attack followed by dehydration reaction (Scheme 2). Pyrazoles have been suggested to exhibit important biological activities and many synthetic routes for preparing pyrazole derivatives have been reported.[8-10] However, kinetics and synthesis of **4** from the reaction of **2** with hydrazine have not been reported. We report a detailed mechanism for the reaction of **2** with hydrazine to yield **4**.



Scheme 1.



Scheme 2.

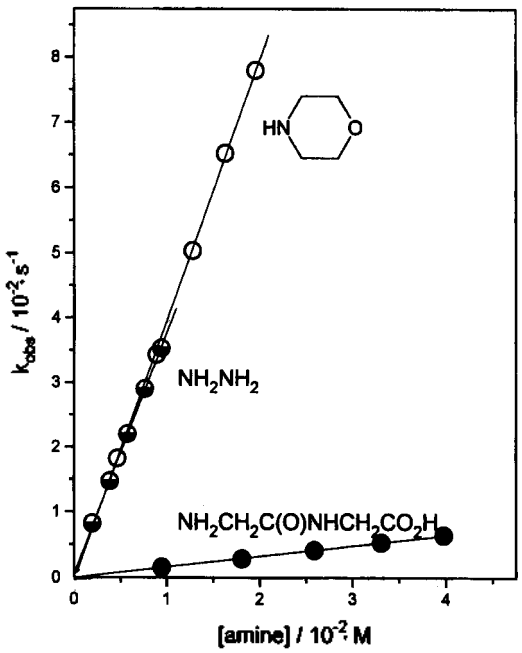


Figure 1. Plots showing dependence of k_{obs} on amine concentrations for the reaction of 3-butyn-2-one (2) with glycylglycine (●), hydrazine (○) and morpholine (○) in H_2O at 25.0±0.1 °C.

Reactions were followed by monitoring the appearance of enamines at a fixed wavelength corresponding to the maximum absorption (λ_{max}) or the disappearance of enamine (**3**) for the formation reaction of **4**. All the kinetic studies were performed under pseudo-first-order conditions in which amine concentrations were in a large excess of **2** in H_2O at 25.0±0.1 °C. Excellent pseudo-first-order kinetics were always observed. Second-order rate constants (k_2) were obtained from the slope of plots of observed pseudo-first-order rate constants (k_{obs}) versus amine concentration (Figure 1). The kinetic results are summarized in Table 1.

As shown in the Table, the basicity of hydrazine is similar to that of glycylglycine, but the former is about 20 times more reactive than the latter. Therefore, it is evident that hydrazine exhibits the α-effect[11] in the present system. However, the α-effect observed in the present *sp* carbon is considered to be unusually small, since the magnitude of the α-effect has been generally observed to increase with increasing the s character of the electrophilic atom in the substrate.[12] For example, the magnitudes of the α-effect were reported to be about 10^1, 10^2 and 10^4 for sp^3, sp^2 and *sp* carbon, respectively.[12] Therefore, the magnitude of the α-effect in the present system is considered to be significantly smaller than would be expected from the hybridization of the electrophilic center.

Steric hindrance has been reported to be significant for the addition of amines to activated acetylenes.[7,13] It is obvious that morpholine would experience more steric hindrance than hydrazine. However, interestingly, morpholine is more reactive than hydrazine, although the latter is an α-effect nucleophile. One might attribute such an absence of the α-effect to the difference in the reaction mechanism between the primary and secondary amines. In order to obtain mechanistic information, we performed the reactions of **2** with morpholine and hydrazine in D_2O. The kinetic results are summarized in Table 1. The magnitudes of the kinetic isotope effect (k^H/k^D, KIE) have been calculated to be 0.95 and 2.36 for the addition of morpholine and hydrazine to **2**, respectively. This contrasting KIE clearly suggests that the addition reaction of morpholine to **2** would

Table 1. Summary of Second-Order Rate Constants (k_2, $M^{-1}s^{-1}$) for Additions of Amines to 3-Butyn-2-one in H_2O at 25.0±0.1 °C

	Amines		
	glycylglycine	hydrazine	morpholine
k_2	0.160	3.66	3.90
pK_a^b	8.25	8.10	8.66

[a] The data in parentheses are obtained from the same reaction run in D_2O. [b] pK_a data from reference 15.

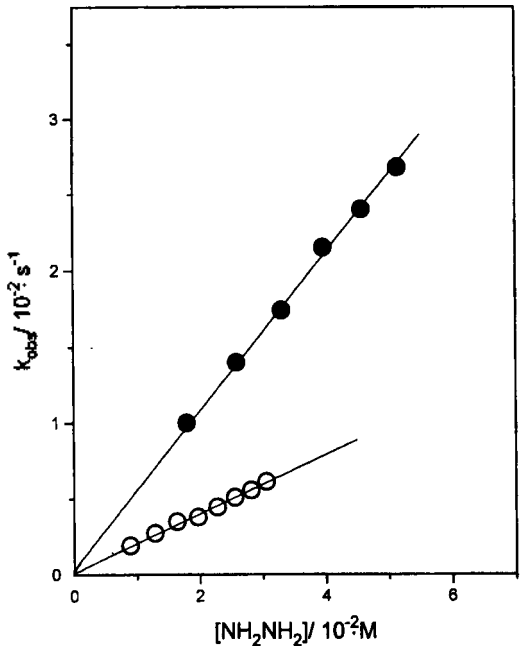
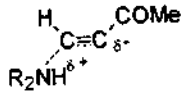
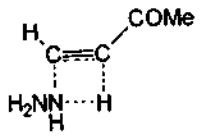


Figure 2. Plots showing kinetic isotope effect for the formation of 3-methylpyrazole (4) from the reaction of 3 with hydrazine in H_2O (●) and D_2O (○) at 25.0±0.1 °C.

proceed in a different mechanism from the corresponding reaction of hydrazine. The inversed KIE for the morpholine system indicates that the nucleophilic attack of morpholine to the acetylenic carbon atom is the rate-determining step (RDS), and the proton transfer occurs rapidly after the RDS (TS1). The fact that deuterated morpholine in D_2O is more reactive than morpholine in H_2O may result from a steric secondary isotope effect on going from the reactants to the transition state.[14] This is fully consistent with the previous proposal that steric effect is significant for the addition reaction of amines to activated acetylenes.[7,13]



TS1



TS2

However, on the contrary, the KIE for the addition reaction of hydrazine to **2** is calculated to be 2.36. Such a primary KIE strongly supports a mechanism in which proton transfer is involved in the RDS, and one can suggest a concerted mechanism for the addition of hydrazine to **2** (TS2). This argument is consistent with the previous report that additions of amines to **1** gave only the syn-addition products, trans-enamines.[7] Therefore, direct comparison of rate constants between the morpholine and hydrazine systems would give no significant meaning due to the difference in the reaction mechanism.

As mentioned in the preceding section, it has been found that the enamine (**3**) formed from the reaction of **2** with hydrazine reacts further to produce 3-methylpyrazole, **4** (Scheme 2). In order to produce **4**, the trans-enamine should isomerize to the *cis*-enamine prior to intramolecular nucleophilic attack by the hydrazine moiety to the carbonyl carbon of the enamine. Such a *cis-trans* isomerization has been reported to occur rapidly *via* a unimolecular reaction.[7] In order to investigate the reaction mechanism, we preformed kinetic studies for the pyrazole formation reaction in H_2O and D_2O with different hydrazine concentrations. The kinetic results are demonstrated graphically in Figure 2. One can find that the observed pseudo-first-order rate constants are linearly related with the hydrazine concentration, indicating that the reaction is not unimolecular reaction, but is catalyzed by hydrazine. Therefore, one can suggest that the intramolecular nucleophilic attack by the hydrazine moeity to the carbonyl carbon of **3** (the first step in Scheme 2) occurs before the RDS and external hydrazine catalyzes the deprotonation (or dehydration) step as a general base catalyst (*via* E2 or E1cb mechanism). This argument can be further supported from the result of KIE. The KIE is calculated to be 2.49 for the formation of **4** from the corresponding enamine in H_2O and in D_2O. The finding of primary KIE in the present system clearly supports that proton transfer is the slow step, and therefore, hydrazine can act as a general base catalyst.

More detailed kinetic and synthetic studies are currently underway using various hydrazine derivatives.

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Magic Angle Spinning NMR Techniques for the Study of Surfactants

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We would like to present our preliminary results of ^{13}C magic angle spinning (MAS)[1] NMR spectra of aqueous surfactant solutions which seem superior to solid state cross polarization (CP)[1]/MAS or regular liquid state NMR spectra in terms of spectral resolution. This improved spectral resolution rendered it plausible to clearly identify chemical species newly formed in the solutions due to mechanical treatment. Our results suggest that MAS NMR technique is very useful to identify molecules not only in aqueous surfactant solutions but also in *highly viscous liquid* samples such as polymer solutions. MAS has been used extensively in solid state NMR to remove line broadening caused by chemical shift anisotropy, first order quadrupole interaction, and dipole interactions.[1,2] Magnetic susceptibility line-broadening of liquid samples as well as of solid state samples was reported to be removed by MAS.[3] Proton MAS NMR techniques were proved to be useful to study emulsions by removing the broadening due to magnetic susceptibility mismatch among phases in multiple emulsions.[4] Recently MAS has been also exploited to remove line-broadening caused by residual dipole interaction from the restricted motions of resin-bound molecules and by magnetic susceptibility mismatch at the boundary of the bead.[5] But this work is the first report on the promising aspect of the application of MAS to highly viscous liquids such as aqueous surfactant solutions and polymer solutions. In these samples, molecular motions are slow enough to have residual dipole interaction resulting in broad NMR linewidths. Discontinuity of magnetic susceptibility at the boundary of micelle and water could be another line-broadening factor in the NMR spectra of aqueous surfactant solutions. These line-broadenings can be got rid of by MAS.

The samples were taken from the experiment on drag reduction. Drag reduction is a fluid mechanical phenomenon in which the pressure drop in a turbulent pipe flow is substantially lowered when a small amount of polymer or surfactant is added to the flowing solvent. Many researches have been directed toward the proper utilization of this effect to its potential benefit in many systems such as district heating and cooling. However the application of drag reduction has been deterred by the loss of drag reducing ability in prolonged use. In the case of surfactant solution, the drag reducing ability is completely lost after a certain period of usage. There are several possible mechanisms for the loss of drag reducing ability : micelle sizes and/or shapes are changed; surfactant molecules are chemically altered; the concentration of surfactants is lowered due to the adsorption onto the pipe wall. In this research we check whether the second mechanism is important. The first and third mechanisms can be checked with other analytical methods and will be presented elsewhere.

The surfactant HABON (Hochest Co.) was used without further purification. Surfactant solution of 2000 wppm was prepared by diluting a master solution of 10 wt %. The solvent was distilled water. The master solution was prepared by dissolving desired amount of HABON in 200 mL distilled water. The surfactant solution was subjected to turbulent pipe flow continuously. A peristalic pump and a plastic tubing were used in the circulation loop. The inner diameter and length of tubing were 4.25 mm and 5.15 m, respectively. The initial Reynolds number based on the solvent viscosity was set at 8,200. Sample I was taken after 26 minutes of circulation. Sample II was taken after 126 hours of circulation at which the drag reducing ability of the surfactant solution is completely lost.

Liquid state ^{13}C NMR spectrum of sample I acquired with the Bruker DPX 300 instrument (Bruker Analytische Messtechnik GmbH, Germany) is shown in Figure 1A. The pulse sequence repetition time and the pulse length were 2.5 sec and 2.7 μs (30 degree flip), respectively. Proton decoupling was continuously on[6] during the NMR experiment. To enhance signal intensity, the sample I was about 10 times concentrated by drying with a vacuum concentrator (Heto Lab. Equipment, Denmark) and dissolving in D_2O. The CP/MAS spectrum of the dried (solid state) sample I in Figure 1B was acquired with the Varian UNITYplus 300 instrument (Varian Associates Inc., U.S.A.) and at the sample spinning speed of 5 kHz. The contact time and the pulse sequence repetition time were 800 μs and 5 sec, respectively. The H_1 field strength was 50 kHz. The MAS spectrum of sample I in Figure 1C was acquired under proton decoupling and at 2.7 kHz spinning speed but without CP. The pulse length and pulse repetition time were 5 μs corresponding to 90 degree flip and 3 sec, respectively. The samples