^{14}N NMR Evidence for Initial Production of NH_3 Accompanied by Alcohol from the Hydrolysis of Ethylamine and Butylamine in Supercritical Water

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A ^{14}N and ^{1}H NMR spectroscopic study was carried out to shed light on the microscopic aspects of the reaction of model alkylamines at a supercritical temperature of 400 °C. It is disclosed that NH_3 and ROH (R = CH_3CH_2 and $CH_3(CH_2)_3$) are initially produced from the hydrolysis of ethylamine and butylamine, respectively. When the water density is doubled from 0.2 g cm^{-3}, the pseudo-first-order reaction rate is markedly enhanced beyond the linear response. It suggests that the transition state of C-N bond cleavage is in a dipolar (ionic) state that can be more stabilized due to the many-body solvation by highly polar water molecules at a higher density.

Keywords: Film Forming Amines, Supercritical Water, Nuclear Magnetic Resonance

Achieving further growth of renewable energy has become an urgent issue to protect the global environment. For the implementation of variable renewable energy (VRE) in the power supply, an efficient combination with the traditional fossil power is practically indispensable to secure the safe and stable supply. Frequent shutting down and starting up of a fossil plant for tuning the supply are demanding operation from the viewpoint of the equipment maintenance because undesirable gaseous corrosives as oxygen and carbon dioxide can be brought into the steam–water cycle. Thus, there have been increasing demands for effective corrosion inhibitors. For the purpose, film forming amines (FFA) have been employed in recent years, and more fundamental research needs for this issue are emphasized, e.g., by The International Association for the Properties of Water and Steam (IAPWS); Technical Guidance Documents (TGDs) on the application of FFA in steam power plants[1] and industrial steam generators.[2] By introducing FFA, a hydrophobic film is formed on the inner surface of tubes for steam–water cycles and it is thought that the film can hinder the contact of corrosives and water to the tube materials.[3, 4]

One of the major concerns about the application of FFA arises from lack of information about the stability of FFA in such severe high-temperature high-pressure conditions and that about product species when FFA degrade. In particular, organic acids are most undesirable products. Moed et al. reported that organic acids were produced from low molecular weight amines (so-called alkalizing amines used to keep the circulating water in a basic condition) in the temperature range of 500−560 °C.[5] An extremely low amount of organic acids on the order of 100 ppb or less were reported to be produced from the 10-ppm reactant. While there have also been reported observations of the decomposition of low-molecular-weight alkalizing amines under hydrothermal conditions including those at lower temperatures of a nuclear reactor around 300 °C,[6–8] the reaction paths, in particular the initial steps, have not been clarified yet. Since there are involved a wide range of thermodynamic states in a steam–water cycle in the power plant, it is essential to clarify the reaction pathways of FFA to confirm the effectiveness and safety.

Ethylamine (EtA, 70 vol% aqueous solution, Nacalai Tesque) and butylamine (BuA, ≥99.0%) were used without further purification. Solvent water was purified using a Milli-Q Gradient A-10 system (Merck Millipore). In this study, ordinary water H_2O was used instead of deuterated water D_2O to avoid the exchange of hydrogens of alkyl chains with deuteriums; this exchange occurs at high temperatures as reported elsewhere.[9, 10] The solution of EtA, prepared at 1.0 mol dm^{-3} under ambient conditions, was injected into a quartz glass tube reactor (2.0 mm i.d. and 4.0 mm o.d.), the air in the gaseous phase was exchanged with argon so that the reaction can be free from O_2 from the air, and the tube was sealed with a gas burner. The density at a supercritical temperature was controlled by adjusting the ratio of the solution injected into the quartz tube reactor under ambient conditions to the inner volume of the reactor; e.g., the supercritical water density is 0.2 g cm^{-3} when the ratio is 0.2. High temperature reaction was carried out by putting the quartz tube reactor into an electronic furnace preheated to a reaction temperature; the temperature was controlled within ± 1 °C. After a reaction time, the reactor tube was taken out of the electric furnace and put into a water bath to quench the reaction.

The reaction products were monitored using ^{1}H and ^{14}N NMR spectroscopy with a JEOL ECA500W spectrometer. For a ^{1}H NMR measurement, a quartz tube reactor was placed into a 5-mm NMR sample tube (5.0 mm o.d. and 4.2 mm i.d.). For a ^{14}N NMR, three reactor tubes were placed in a 10-mm NMR sample tube (10.0 mm o.d. and 9.0 mm i.d.). The space between the quartz tube(s) and the NMR sample tube was filled with DMSO-d6 used for ^{2}H locking. The ^{1}H signal of water was suppressed by DANTE presaturation.[11] The ^{1}H chemical shift was externally referenced to the methyl proton of sodium 3-(Trimethylsilyl)propionate-2,2,3,3-d4 (TMSP-d4, 0.000 ppm) in an aqueous solution which was placed in the same geometry as that of the aqueous amine solution. The ^{14}N NMR (36 MHz at 11.7 T magnet) spectra were measured using a probe for the low-frequency nuclei (JEOL T10L). The ^{1}H and ^{14}N signals were accumulated for 16 and 4096 times, respectively, to attain a good signal-to-noise ratio.

The gas NMR was measured for ^{1}H and ^{13}C nuclei by placing the sample tube upside down; the inner diameter of 2.0 mm is narrow enough to keep the liquid phase remaining

in the upper side due to the surface tension during the measurement.[10] The ^{1}H and ^{13}C signals were accumulated for 16 and 16384 times, respectively. In the measurement of the gas phase, liquid products on the inside wall of the quartz tube were observed in addition to the gaseous products. The gaseous products were distinguished from liquid ones according to the diffusivity (difference in 3 orders of magnitude in self-diffusion coefficients between gas and liquid phases) measured by using the pulsed-field-gradient spin-echo method.[12, 13]

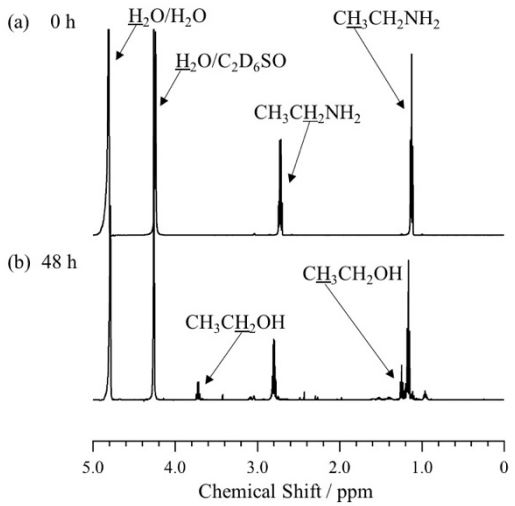

Figure 1. ^{1}H NMR spectra of the aqueous solution of EtA (a) before the supercritical water reaction (reaction time of 0 h) and (b) treated at 400 °C for 48 h at 0.20 g cm^{-3}. In (a) the peaks at 1.16 and 2.80 ppm are assigned to the methyl and methylene protons of the reactant EtA, respectively, the peaks at 4.79 ppm (distorted by water suppression) to the solvent water, and the peak at 4.26 ppm to the impurity water in DMSO-d6. In (b) the peaks at 1.25 and 3.72 ppm are assigned to the methyl and methylene protons of the product EtOH, respectively.

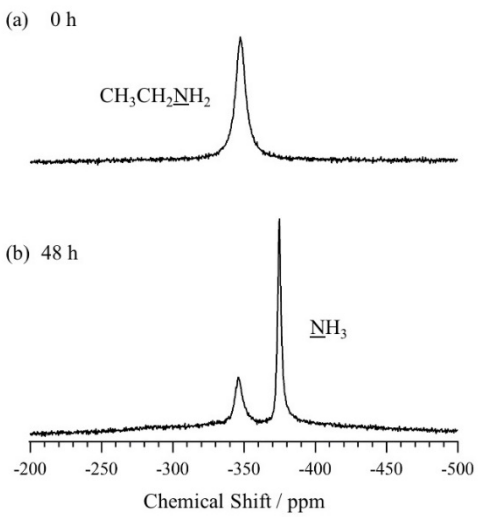

Figure 2. ^{14}N NMR spectra of the aqueous solution of EtA (a) before the supercritical water reaction (reaction time of 0 h) and (b) treated at 400 °C for 48 h at 0.20 g cm^{-3}. The peaks at −346 and −375 ppm are assigned to EtA and NH_3, respectively.

Quantitative determination of the reaction products as functions of time and conditions is the most important first step for the kinetic study. Figure 1 shows how the ^{1}H NMR spectra changes after a 48-h reaction at a supercritical temperature of 400 °C and at a density of 0.2 g cm^{-3}, and how the observed signals are assigned. It is found that EtOH is initially produced, so the hydrolysis of the N-H bond of EtA can be considered to occur as follows:

$$C_2H_5NH_2 + H_2O \rightarrow C_2H_5OH + NH_3 \qquad (1)$$

To make sure this reaction pathway, we need to confirm the counter species of C_2H_5OH, i.e., NH_3 that cannot be detected however by ^{1}H NMR due to the rapid proton exchange. For the purpose, we applied the ^{14}N NMR spectroscopy by overcoming the low sensitivity. Figure 2 shows the ^{14}N NMR spectra taken under the same reaction conditions as those of Figure 1. After the reaction, there is clearly observed a signal for NH_3. The NH_3 signal is sufficiently separated for the quantitative analysis from that for the amino residue of EtA; the two signals are deconvoluted into two Lorentzian peaks.

Now let us examine whether any other reactions take place in addition to eq 1. As seen in Figure 1b, there are various weak peaks besides the EtOH ones. This indicates that the hydrothermal reaction expressed by eq 1 is initially dominant but not exclusive during the long reaction time. To understand this more, we show the time evolution of the concentration of the reactant and products of EtA treated at 400 °C for 72 h at 0.20 g cm^{-3} in Figure 3. When we pay attention only to the reactant EtA and one of the products NH_3 we can see the reaction of the amino moiety is rather simple. The amounts of EtA determined by the ^{1}H and ^{14}N NMR spectroscopic methods coincide with each other within the experimental uncertainties (~10%). The decrease of the reactant EtA and the increase of NH_3 are approximately in one-to-one correspondence; the sum of EtA and NH_3 corresponds to the mass balance determined by ^{14}N NMR, which is roughly kept at unity. A slight decrease in the mass balance, ranging to 10%–20%, can be ascribed to the adsorption of amino residue of EtA onto the inner surface of the quartz tube. The reasonably good mass balance with respect to ^{14}N indicates that eq 1 dominates the amino group reaction; there are some minor heterogeneous side-reactions as mentioned above.

In contrast to the amino group, the ethyl has complicated hydrothermal reaction pathways besides eq 1. Figure 1 exhibits several ^{1}H signals besides EtOH in the liquid phase. Although at present the individual assignment is difficult due to the signal overlapping, the group assignment is possible in view of the high-field chemical shifts. There were also several unassigned signals observed in the gas phase as seen in Figure S1 in Supporting Information. We can determine the yields of the unknown (UK) products to confirm the validity of the overall mass balance under the assumption that the number of protons of a product species originating from one reactant EtA molecule is five. In the methyl-proton region (0.9–1.7 ppm) in the liquid phase, where signals overlap most severely, the amount of the intensities of methyl

protons of EtA and EtOH were estimated based on their methylene protons that are more separated, and the intensities of the UK peaks can be obtained by subtracting those of EtA and EtOH from the integral intensity of the whole methyl-proton region. The amounts of the UK thus determined are plotted in Figure 3. The sum of the reactant and the products are shown as the ^{1}H mass balance. The mass balance is approximately kept unity as in the case of the ^{14}N mass balance, which verifies the validity of the assumption used to quantify UK. This means that the conversion from less exchangeable protons, such as methyl, to the exchangeable one, such as hydroxyl, is not significant and almost negligible in the analysis of the product yields. The UK in both phases increase until 48 h, and after that, the UK in the liquid phase *decrease* and those in the gas phase *increase*, showing that the products in the liquid phase are intermediate ones that are subsequently converted into gaseous ones with the mass balance kept. For further assignment of the UK, an intensive, high sensitivity ^{13}C NMR can be done with an enriched sample and/or two-dimensional measurements are needed.

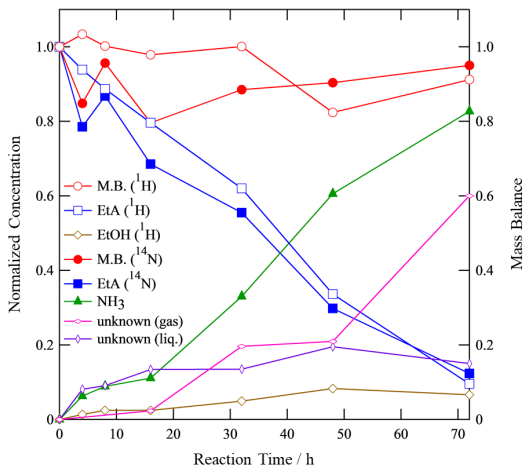

Figure 3. Time evolutions of the concentrations of the reactant and products for the reactions of ethylamine at 400 °C and at 0.20 g cm^{-3}. The vertical axis on the left shows the normalized concentration, and that on the right shows the mass balance. The normalized concentration denotes the concentration of the compound of interest divided by the initial substrate concentration. The mass balance denotes the ratio of the sum of the amount of nitrogen or proton atoms in the reactant and the products detected by ^{14}N or ^{1}H NMR at each reaction time divided by the amount of the corresponding nucleus of the reactant in the beginning of the reaction.

Now let us examine the effect of the water density. The time evolutions of the reactant and products at 0.40 g cm^{-3} are shown in Figure S2 in Supporting Information, for which the reaction temperature and the molality of EtA are set to be the same as those for Figure 3. It is seen that the decrease of EtA and the increase of NH_3 become significantly faster when the water density is doubled. For the quantitative comparison, we fitted the concentration of ethylamine to pseudo-first-order kinetics, $d[EtA]/dt = -k[EtA]$, where [EtA] is the concentration of ethylamine and k is the pseudo-first-order reaction rate constant. The k values thus determined at 0.20 and 0.40 g cm^{-3} are $(6.6 \pm 0.7) \times 10^{-6}$ and $(3.4 \pm 0.5) \times 10^{-5}$ s^{-1}, respectively. The rate is enhanced by a factor of (5 ± 2), much larger than the density increase. The increase of the rate constant overwhelms the proportionality to the water density, implying that the crowding of water molecules around the reactant promotes the cleavage of the amino residue from the reactant amine in the hydrolysis reaction. The acceleration due to water suggests that the barrier-crossing transition state is in a polar or ionic state, which can be more stabilized by electrostatic interactions at higher densities. Further comprehensive theoretical and experimental investigations are required concerning the effect of size and hydrophilicity/hydrophobicity of functional groups in the reactant amines.

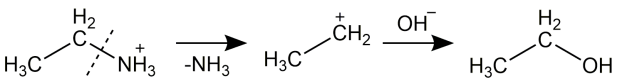

Figure 4. Proposed mechanism of the hydrolysis C-N bond cleavage of EtA in supercritical water.

The dramatic influence of the supercritical water density found here leads us to such a mechanism for the hydrolytic cleavage of the C-N bond of EtA in supercritical water as illustrated in Figure 4. First, the amino group of EtA is protonated through the contact with water molecules and then the C-N bond is polarized and broken to release NH_3. The fragment CH_3-CH_2^+ immediately binds to a neighboring hydroxide ion to produce CH_3CH_2OH; otherwise, it binds back to -NH_3^+ as the reverse reaction. In this mechanism, the elongation of the C-N bond to produce the unstable fragment CH_3-CH_2^+ is the rate-determining step. The assumption of an ionic species in the transition state is consistent with the experimental observation that the reaction is dramatically accelerated by the increase in the water density; the ionic species, as well as polar ones, will be more stabilized by lowering the solvation free energy at a higher water density in supercritical states.[14] Elimination of NH_3 from neutral EtA is unlikely to occur because the counter species ethene is not observed in the gas-phase ^{1}H and ^{13}C NMR spectra (Figure S1 in Supporting Information). It is plausible that the UK species are produced by the reaction of ethanol. The reaction of ethanol in supercritical water in a quartz glass reactor tube was reported by Arita et al.[15] and the major product species reported were hydrogen, methane, ethane, and acetaldehyde, none of which are observed in our present study as seen in Figure S1. The difference in the product species could be attributed to the basicity, and an investigation of this point will be of particular interest in relation to steam–water cycles whose circulating water is kept being basic for controlling corrosion. For FFA applications, the important issue is to what extent the products contain acidic species. We measured the pH value of the aqueous phase at room temperature after the high-temperature reaction. The pH values for the sample treated for 4, 8, and 16 h at 400 °C and at 0.40 g cm^{-3} were 11.9, 12.0, and 10.7, respectively. While there observed a

slight downward shift at 16 h, the pH value remains satisfactorily in basic conditions. This means that the production of acidic species is, if any, not the dominant determining factor of the pH due to the overwhelming NH_3. Thus, the NH_3 production is efficient for suppressing the corrosion through the pH control.

Now let us examine the effect of the alkyl chain length of the reactant amines. To the end, we examined the decomposition of butylamine (BuA) at 400 °C and at 0.20 g cm^{-3} for the comparison with that of EtA described above. Examination by ^1H NMR showed that BuA decomposes about three times faster than EtA; a pseudo-first-order reaction rate constant for BuA is $(2.0 \pm 0.4) \times 10^{-5}$ s^{-1}. In the product species, butanol (BuOH) was observed as the hydrolysis product in parallel with eq 1; the amount of produced BuOH was smaller by 10%−30% than that of the consumed reactant BuA as in the case of EtA. The similarity in the product distribution between EtA and BuA suggests that the reaction pattern like eq 1 is common to alkylamines whatever the chain length is. In supercritical states, there would be more microscopic inhomogeneity of hydrophilic and hydrophobic moieties of alkylamines when the alkyl chains are longer.[16] In supercritical states where there is larger density inhomogeneity, hydrophilic and hydrophobic moieties could enhance localization of reactant water molecules around hydrophilic amino residues, leading to the stabilization of the transition state. To have molecular insights into the reaction mechanism of the hydrolysis of amines in supercritical conditions, we need to do a more comprehensive and systematic kinetic analysis as a function of key parameters such as the alkyl chain length and a reactant concentration.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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Graphical Abstract

Textual Information

A brief abstract (required)	The reaction of alkylamines at a supercritical temperature of 400 °C was studied using a multinuclear NMR spectroscopy. It was revealed for the first time that the initial step is the hydrolysis cleavage of the C-N bond to produce ammonia. The reaction mechanism is proposed based on the effect of the water density as illustrated.
Title(required)	^{14}N NMR Evidence for Initial Production of NH_3 Accompanied by Alcohol from the Hydrolysis of Ethylamine and Butylamine in Supercritical Water
Authors' Names(required)	Ken Yoshida, Haruka Yoshioka, Natsuko Ushigusa, and Masaru Nakahara

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