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Decomposition of acetamide and formamide in pressurized hot water

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Acetamide and formamide were individually decomposed in a pressurized hot water in a tubular flow reactor at temperatures from 573 to 693 K, and pressure of 23 MPa, residence times up to 500 s, and the initial concentrations of both amides from 0.005 to 0.5 mol/L. The major products were ammonia and acetic acid from decomposition of acetamide, and ammonia and formic acid from that of formamide. Formic acid was further decomposed readily into carbon dioxide. Although the decomposition reactions for both amides were represented acceptably by the first order reaction kinetics, the rate constants increased with increasing the initial sample concentrations due to the autocatalytic effect. Apparently the second order reaction kinetics with respect to the concentration of each amide remained more represented the global decomposition rates, and the rate constants decreased with increasing the initial concentrations. The effects of hydrogen peroxide added on the global decomposition rates and the product yields were not evident: the addition slightly lowered the rates, but the major products were almost the same as those in the absence of hydrogen peroxide at temperatures lower than 653 K. Above 653 K more CO_2 was produced.

1. Introduction

High-temperature and high-pressure water has received attention as roles of a solvent and a reactant in decomposition of organic pollutants contained in wastewaters. In fact, catalytic and non-catalytic decompositions of organic compounds in aqueous solutions have extensively been studied under sub- and supercritical conditions of water in the absence and the presence of an oxidant, as reviewed [1–3]. In particular, the decomposition of organic compounds containing nitrogen is important for wastewater treatment. While a large number of studies on the decomposition of nitrogen-containing compounds have been made under sub- and supercritical conditions [2–10], those on the decomposition of amides are limited [2, 3, 8–10]. Lee and Gloyna [8] carried out decomposition of acetamide at 671 to 803 K at the initial amide concentrations from 0.00023 to 0.012 mol/L in a tubular flow reactor, and evaluated hydrolysis and oxidation kinetics associated with the destruction of acetamide under supercritical conditions of water. Izzo *et al*. [9, 10] also studied the kinetics of amide decomposition as intermediate products from the decomposition of various nitriles using batch reactors.

In the previous studies on amide decomposition in sub- and supercritical water, the amide concentrations fed are relatively low or the data on the rates and the product yields are available in the limited range of the reaction conditions. Thus, in the present study the decompositions of acetamide and formamide were separately carried out in a plug flow reactor over the wide range of amide feed concentration with and without hydrogen peroxide. The yields of the major products were measured, and the decomposition rates were determined.

2. Experimental apparatus and procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reaction was carried out isothermally at temperatures ranging from 573 K to 693 K and constant pressure of 23 MPa. A preheating column (0.5 mm i.d. × 2 m long) and a tubular reactor (0.5 mm i.d.× 5 m long or 2.17 mm i.d. × 6 m long), both made of stainless-steel

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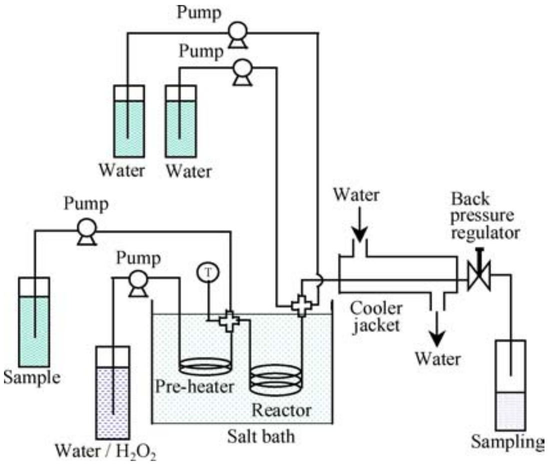

Figure 1 Schematic diagram of the experimental apparatus.

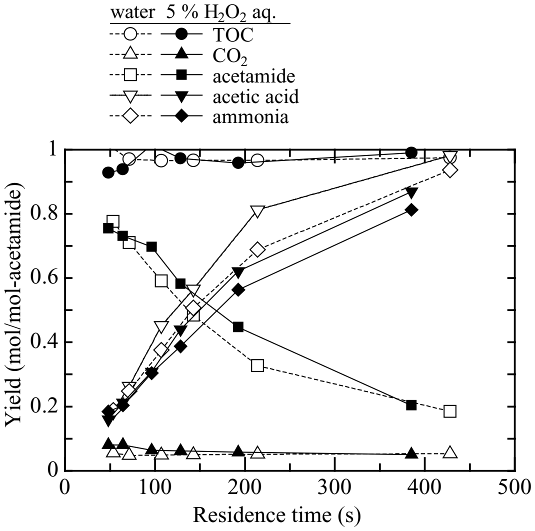

Figure 2 Time change dependences of product yields, quantites of TOC and acetamide remained at 593 K and the initial concentrations of 0.5 mol/L in the presence and the absence of hydrogen peroxide.

tubing, were immersed in a molten salt bath, equipped with a stirrer, and heated by an electric furnace. The temperature of the bath was maintained at the prescribed value within ± 1 K. Prior to feeding an aqueous solution of amide (acetamide, purity of 98%, or formamide, 98%, both obtained from Kanto Chem. Co., Tokyo, Japan) to the reactor, the solution and distilled water were degassed for about 15 min by ultrasonic wave, and then it was supplied mainly at 0.5 mol/L and room temperature directly to the tubular reactor immersed in the bath by a HPLC pump (Model L-6000, Hitachi, Japan). The temperatures of the inlet and the outlet of the reactor were measured with the thermocouples attached to the reactor. In addition, by measuring the fluid temperatures at the exits of the reactors having different lengths with a thermocouple installed in a cross-connector, the solution temperature was found to have reached the prescribed value at the positions longer than 0.3 m from the reactor inlet. A hydrogen peroxide aqueous solution or distilled water, fed by a syringe pump (Model DM100, ISCO, U.S.A.) to the preheating column immersed in the bath, was mixed at the cross-connector with an aqueous amide solution fed separately on the same axis but in the opposite direction. Note that hydrogen peroxide was found to be completely decomposed at the inlet of the reactor by analyzing the solution collected at the inlet. In order to quench the solution at the exit of the reactor, cold distilled water was added to the eluted solution.

The pressure of the system was controlled by a back pressure regulator, which is capable of controlling the pressure within ± 0.1 MPa with a high frequency open-shut valve operated electro-magnetically. After the system had reached the steady state conditions, the solution eluted from the exit of the back pressure regulator was collected periodically, and analyzed.

The yields of amides and acids were measured by a HPLC. Nitrate and nitrite ions were analyzed by ion chromatography. The ammonia yields in terms of NH_4^+ were determined by a capillary electrophoresis apparatus (CAPI-3300, Otsuka Electronics Co., Japan). Total organic carbon and total nitrogen contents were also measured by a TC and TN analyzer (Model TOC-V, Shimadzu, Japan).

3. Results and discussion

3.1. In the absence of oxidant

Fig. 2 shows the time dependence of the product yields and TOC value from decomposition of acetamide, together with the quantity of acetamide remained at 593 K in the absence and the presence of hydrogen peroxide. The description on those with H_2O_2 is made in the next section. The major products were acetic acid, ammonia, and carbon dioxide. While the quantity of acetamide remained decreased with time, the TOC values were nearly 97 % over the whole range of residence time. Thus, in the decomposition of acetamide, acetic acid and ammonia were quite selectively produced, and the yields of acetic acid were roughly equal to that of ammonia at each residence time. The yield of carbon dioxide was as low as 0.05 mol/mol-acetamide loaded initially over the entire range of the residence time. Acetic acid and ammonia, which are the major products, and quite stable under the conditions, as pointed out by many investigators, e.g., Savage [1]. Fig. 3 plots yields of (a) ammonia and (b) acetic acid vs. the quantity of acetamide remained at various temperatures and residence times with and without hydrogen peroxide. In case of the addition of H_2O_2 the results are mentioned in the following section. Over the entire range of

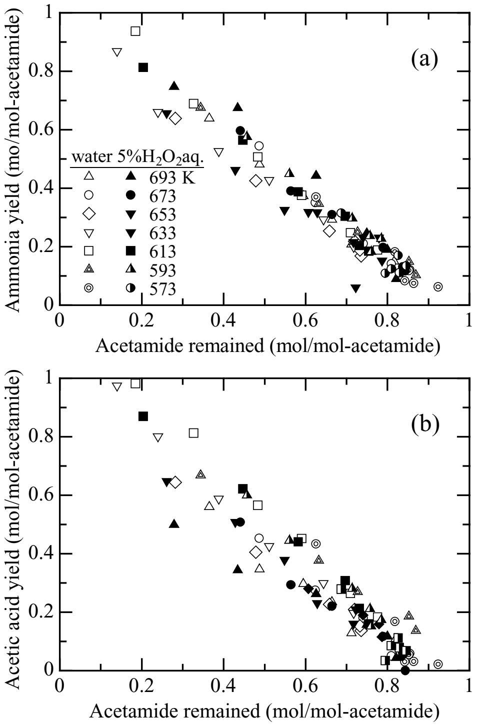

Figure 3 Yeild cross-plots for (a) ammonia and (b) acetic acid vs. acetamide remained at various temperatures in the presence and the absence of hydrogen peroxide.

temperature studied from 573 K to 693 K, the yield data for acetic acid and ammonia were strongly correlated with the quantity of acetamide remained, roughly irrespective of temperature.

Fig. 4 shows C/C_0 for acetamide vs. residence time in a semi-logarithmic plot, where C_0 and C were concentration of fed initially and that at residence time t, respectively. As depicted, the global rates of the acetamide decomposition seemed to be represented by the first order reaction kinetics.

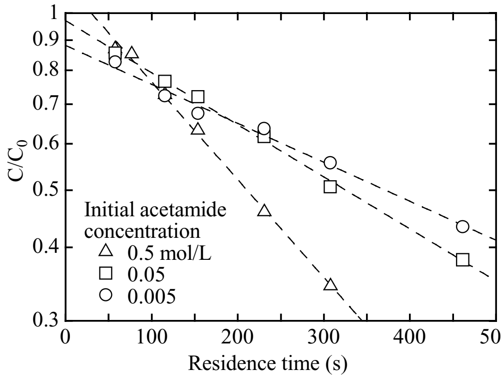

Figure 4 C/C_0 for acetamide vs. residence time at various initial concentrations of acetamide at 593 K.

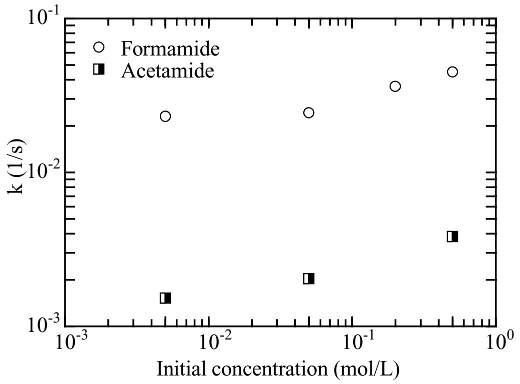

Figure 5 Effect of the initial concentration on the first order rate constants for both amides at 593 K.

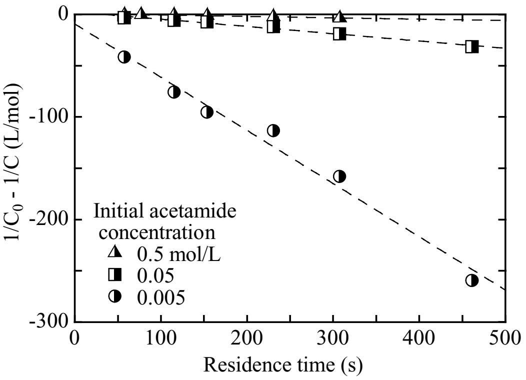

Figure 6 $(1/C_0 - 1/C)$ for acetamide vs. residence time at 593 K and various initial concentrations.

Fig. 5 plots the dependences of the initial concentration on the first order rate constants determined for acetamide and formamide at 593 K. At concentrations higher than 0.05 mol/L the rates for both compounds evidently increase with increasing initial concentration. Although the first order reaction kinetics acceptably represented the decompositions of the amides at each initial concentration, the rate constants showed the dependence of the initial concentration. Thus, the validity of the second order reaction kinetics was also examined. Fig. 6 plots $(1/C_0 - 1/C)$ vs. residence time at various initial concentrations of acetamide at 593 K without hydrogen peroxide. As depicted, the decomposition rates were well represented by the second order reaction kinetics with respect to concentration of each amide remained, as given by Eq (1).

$$\frac{1}{C_0} - \frac{1}{C} = -kt \tag{1}$$

where k is the second order rate constant.

Fig. 7 indicates the initial concentration dependences for acetamide and formamide on the second order rate constants at 593 K. The rate constants for each amide decreased with increasing each initial concentration with

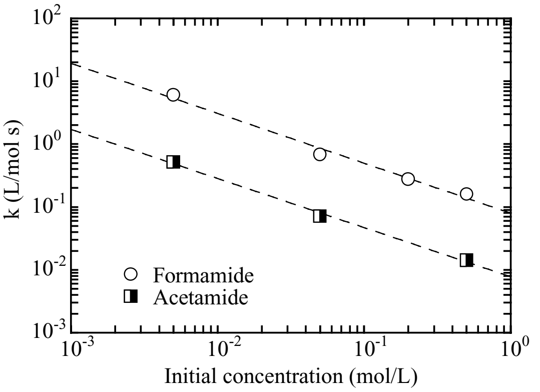

Figure 7 Effect of the initial concentration on the second order reaction rate constants for both amides at 593 K.

the almost same slope of −0.8. The rates for formamide are nearly 10 times higher than those for acetamide.

Fig. 8 plots ($1/C_0 - 1/C$) vs. residence time for acetamide at various temperatures and the initial concentration of 0.5 mol/L. As depicted, the decomposition of acetamide was represented by the second order reaction kinetics over the entire range of temperature. As seen for acetamide decomposition, that of formamide was also represented by the second order reaction kinetics, while it is not shown.

3.2. In the presence of oxidant

The effects of the addition of hydrogen peroxide on the product yields and the quantities of TOC and acetamide remained at 593 K are shown in Fig. 2, as compared with those without an oxidant. The products were the same as those without an oxidant, and the product yields were not drastically changed. As seen in cases without an oxidant, more than 97% of carbon for products measured with the oxidant was obtained in the solution over the entire range of residence time. It is interesting that the conversions of acetamide with the oxidant were slightly lowered, as compared with those without the oxidant. The presence of oxygen probably retards hydrolysis reaction of acetamide in the temperature range studied. Note that the residence times of the fluid were estimated by taking into account the volume change due to oxygen from hydrogen peroxide, under the assumption that hydrogen peroxide was completely decomposed into oxygen and water, as pointed out by Oshima *et al.* [11]. When the volume change is not considered, the residence times increase roughly up to 10%.

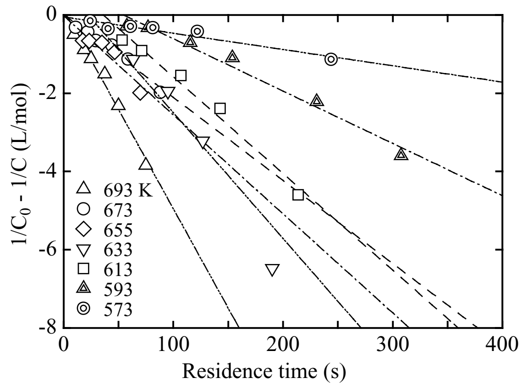

Figure 8 ($1/C_0 - 1/C$) for acetamide vs. residence time at various temperatures and initial concentration of 0.5 mol/L.

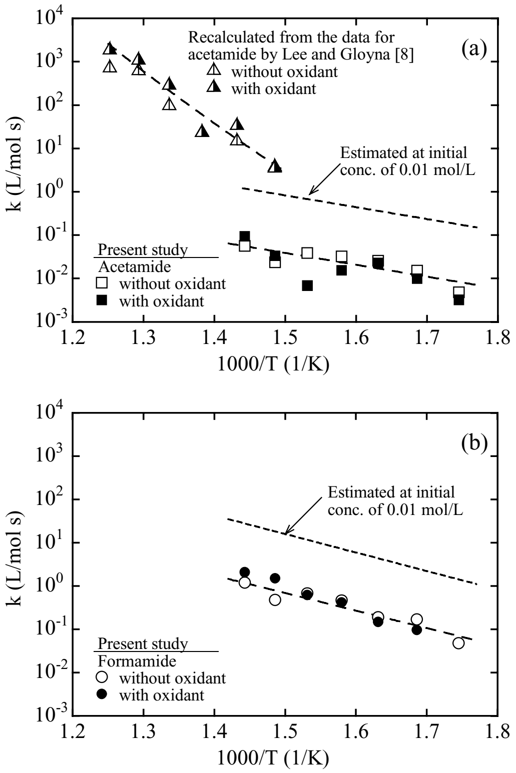

Figure 9 Arrhenius plots for (a) acetamide and (b) formamide both at the initial concentrations of 0.5 mol/L, together with those recalculated from the conversion data for acetamide by Lee and Gloyna [8].

Yields of (a) ammonia and (b) acetic acid vs. acetamide remained at various temperatures and residence times with and without an oxidant are plotted in Fig. 3. The yields of both products were strongly correlated with the quantities of acetamide remained, and the correlations were not significantly affected by the presence of the oxidant.

Fig. 9 shows the Arrhenius plots of the second order rate constants for (a) acetamide and (b) formamide both at the initial amide concentrations of 0.5 mol/L in the presence and the absence of hydrogen peroxide, as compared with those for acetamide, recalculated from the yield data obtained by Lee and Gloyna [8], who had determined the first order reaction rates. The stoichiometric molar ratio of oxygen to acetamide is nearly four, when oxygen was assumed to be produced from complete decomposition of hydrogen peroxide. While the recalculated rates of Lee and Gloyna [8] at the initial concentrations from 0.00023 to 0.012 mol/L are higher than those in the present study, those estimated at 0.01 mol/L from the present data seem to reach the extension of the recalculated data of Lee and Gloyna. The rates for formamide were also plotted in Fig. 9(b), together with those estimated at the initial concentration of 0.01 mol/L. The slopes were almost the same for both amides in the present study, and the rate constants for formamide were more than 10 times higher than those for acetamide. The values significantly increased above the critical temperature of water, while those were slightly increased below the temperature. The pre-exponential factor and the activation energy for acetamide were obtained to be 4.8×10^2 L/(mol·s) and 52 kJ/mol, respectively, at temperatures from 573 to 693 K, and the initial concentration of 0.5 mol/L without an oxidant. Those for formamide were also determined to be 8.2×10^5 L/(mol·s) and 78 kJ/mol at the initial concentration of 0.5 mol/L.

Although the global rates were well expressed by the second order reaction kinetics for acetamide and formamide, the interpretation is difficult. According to Lee and Gloyna [8], the hydrolysis rate can be expressed as:

$$\text{hydrolysis rate} = \left(k_{H^+}\left[H^+\right] + k_{OH^-}\left[OH^-\right]\right) \times [\text{acetamide}] \tag{2}$$

From the dissociation constants of ammonia and acetic acid under hydrothermal conditions, estimated by Izzo *et al*. [9], ammonia is almost completely dissociated, but acetic acid is not. Thus, the solution becomes more basic as the reaction proceeds. The second term in Eq. 2 is more significant when the reactant concentration and/or the conversion are higher. Consequently, the contribution of the second term in Eq. 2 increases with the axial distance of the reactor from the inlet. Thus, in the determination of the global rates for decomposition of amides with/without an oxidant, the concentrations of ions such as H^+, OH^- and $NH_4{}^+$ as well as those of products are required and the further studies are needed.

4. Conclusions

The two amides, formamide and acetamide, were decomposed in water at temperatures from 573 K to 693 K and pressure of 23 MPa in a plug flow reactor at residence times of the fluid from 1 to 500 seconds, and the initial concentrations of each amide from 0.005 to 0.5 mol/L. Apparently the decomposition rates for both amides were more represented by the second order rather than the first order reaction kinetics with respect to the concentration of each amide remained with and without an hydrogen peroxide. The activation energies and the pre-exponential factors for acetamide and formamide at the initial amide concentrations of 0.5 mol/L were determined to be 52 kJ/mol and 4.8×10^2 L/(mol·s) and 78 kJ/mol and 8.2×10^5 L/(mol·s), respectively, without an oxidant. The addition of an oxidant, i.e. hydrogen peroxide, slightly decreased the decomposition rates, and did not affect the product distribution remarkably.

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