

Hydrazine degradation by ultrasonic irradiation

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Available online 24 April 2007

Abstract

The influence of pH on the degradation of hydrazine with a concentration of 0.1 mmol/L was investigated under the stirring (300 rpm) and ultrasonic irradiation conditions (200 kHz, 200 W) in the pH range of 1–9. It was found that the hydrazine degradation depended greatly upon pH under the ultrasonic irradiation condition, while it did not take place over the whole pH range under the stirring condition. Although it has been known that OH radicals and hydrogen peroxide are sonochemically formed from water, it was considered that the OH radicals played an important role of the hydrazine degradation, but not hydrogen peroxide. The pH dependence of the hydrazine degradation was discussed in terms of the relationship between the chemical structure and the basic dissociation constants of hydrazine.

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Keywords: Degradation; Hydrazine; Hydroxyl radical; Stirring; Ultrasound

1. Introduction

Hydrazine (N₂H₄) is manufactured from the chemicals such as ammonia, dimethylamine, hydrogen peroxide, or sodium hypochlorite. The amount of hydrazine produced in Japan in 1995–2000 has been reported to be in a range from 13,000 to 18,000 t per year. Hydrazine has been used as fuel for many rockets and spacecraft, and is used to reduce a corrosion of a boiler, also to make medicines, farm chemicals, and plastic foams. However, it is known that hydrazine injures lungs, liver, kidney, and central nervous system [1]. In addition, the International Agency for Research on Cancer (IARC) has claimed that hydrazine is possible to be carcinogenic to humans.

A number of studies have been conducted on the application of ultrasound to the degradation of environment pollutants in water: for example, polycyclic aromatic hydrocarbons [2], parathion [3], hydrogen sulfide [4], chlorinated hydrocarbons [5,6], fluoro compounds [7,8] and diverse phenols [9,10]. It has been reported that the chemical effects of ultrasound result from the phenomenon of acoustic cavitation [4,11].

Although it has been reported that various types of environmental pollutants can be sonochemically degraded without chemicals, to our knowledge, there are no reports about sonochemical degradation of hydrazine. In this study, we have investigated the effect of ultrasonic irradiation on the hydrazine degradation. Furthermore, influence of pH on the degradation of hydrazine has been studied in order to find more efficient conditions.

2. Experimental

2.1. Sample solutions

The effect of pH on the hydrazine degradation (0.1 mmol/L) was investigated, where the pH of the hydrazine solution was adjusted with addition of hydrochloric acid. The pH of solution was measured with a pH meter (Yokogawa PH72).

All reagent grade chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The water purified by an Organo Purelite PRB-002A was used (resistivity >10⁷ Ω cm).

2.2. Apparatus

Fig. 1 shows the experimental apparatus system. The ultrasonic apparatus consisted of a multiwave ultrasonic generator (Kaijo 4021, Lot. No. 54H5) and a barium titanate oscillator

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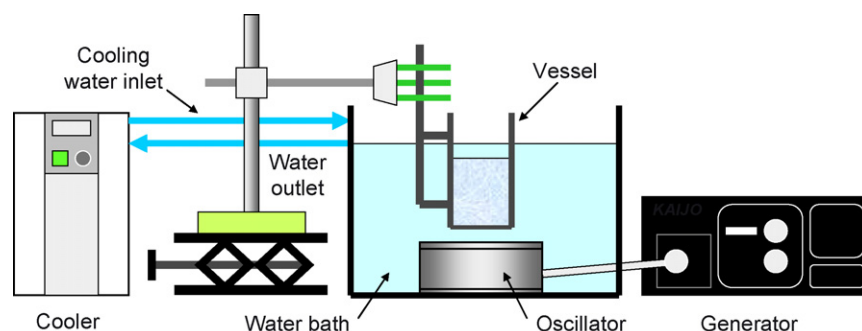


Fig. 1. Schematic diagram of the experimental apparatus system for ultrasonic irradiation.

(Kaijo 4611, Lot. No. 68J3) of 65 mm in diameter, which was operated at 200 kHz with an input electric power of up to 200 W. Hydrazine solution (100 mL) was sonicated in a cylindrical glass vessel of 50 mm in diameter with a total volume of 180 mL under air atmosphere. The bottom of the vessel was planar and made as thin as possible (1 mm) because transmission of ultrasonic waves increases with decreasing the thickness of the bottom. The vessel was mounted at a constant position relative to a nodal plane of the sound wave (3.8 mm: a half of wavelength from the oscillator), and immersed into the water bath, which was cooled by an external cooler (Sibata C-305) and kept at a constant temperature of 20 °C.

Stirring experiments were carried out using an AS ONE DP-1S with a stirring bar (40 mm). The stirring speed was 300 revolutions per minute (rpm).

2.3. Analysis

The concentration of hydrazine during ultrasonic irradiation was determined by the adsorption spectrophotometry method based on Japanese industrial standards [12]. Sample solution including hydrazine was adjusted to acid condition with hydrochloric acid solution before the coloring with *p*-dimethylaminobenzaldehyde. The absorbance of the colored sample solution was measured with a Hitachi spectrophotometer U-2800, where a wavelength of 458 nm was used.

3. Results

3.1. Effect of ultrasonic irradiation

Hydrazine degradation was investigated under the stirring and ultrasonic irradiation conditions. Fig. 2 shows the relationships between the residual concentration of hydrazine and ultrasonic irradiation time or stirring time in the solutions with a concentration of 0.1 mmol/L at pH 8.4. It was found from Fig. 2 that the hydrazine degradation took greatly place under the ultrasonic irradiation condition, but not under the stirring condition. This means that the hydrazine degradation was greatly accelerated by ultrasonic irradiation, where the slope of the line is an initial rate of hydrazine degradation expressed as v_1 . In this study, we use the initial rate of degradation to discuss the obtained data.

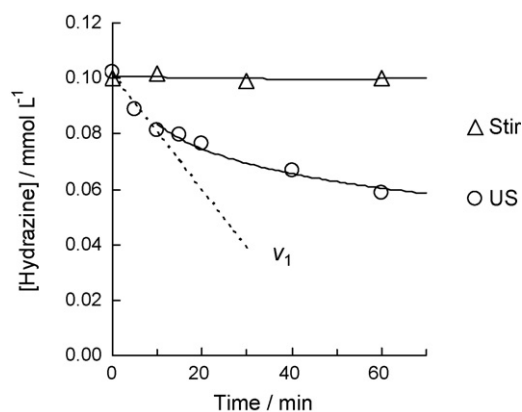


Fig. 2. The change in residual concentration of hydrazine as a function of ultrasonic irradiation time or stirring time in solution with a concentration of 0.1 mmol/L at pH 8.4. v_1 : initial rate.

3.2. Influence of pH

Fig. 3 shows the change in the residual concentration of hydrazine as a function of ultrasonic irradiation time in the solutions at various pHs with a concentration of 0.1 mmol/L. It was found that v_1 was significantly dependent upon pH: the rate of degradation was in the order of pH 1.0 > 8.6 > 4.0. On the other hand, the hydrazine degradation did not occur at any pH under the stirring condition.

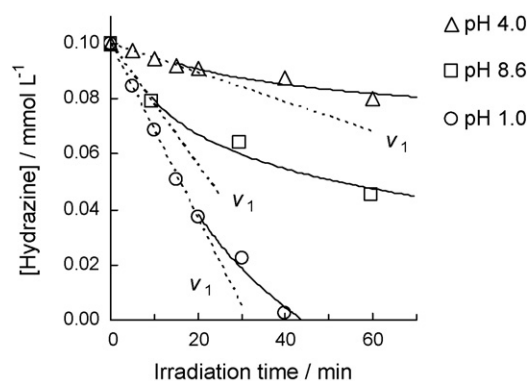


Fig. 3. The change in residual concentration of hydrazine as a function of ultrasonic irradiation time in solution with a concentration of 0.1 mmol/L at various pH.

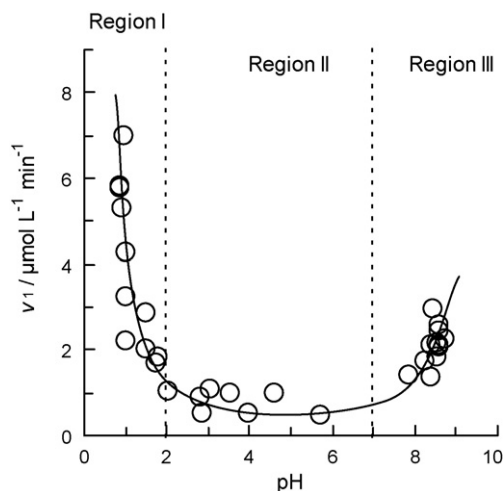


Fig. 4. Initial rate (v_1) of hydrazine degradation as a function of pH under ultrasonic irradiation condition in solution with a concentration of 0.1 mmol/L.

Fig. 4 shows v_1 as a function of pH in the solution with a concentration of 0.1 mmol/L under the ultrasonic irradiation. The v_1 decreased significantly with the increase in pH up to two (Region I), kept constant independent of pH (pH 2–7, Region II) and then began to increase with increasing the pH (Region III). Thus, the pH dependence of v_1 was found to be divided into three regions.

4. Discussion

4.1. Effect of OH radicals on hydrazine degradation

It has been reported that OH radicals and hydrogen peroxide are sonochemically formed from water as shown below [13],

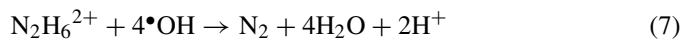
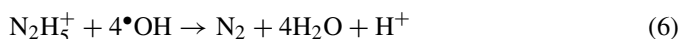


It is generally recognized that chemicals in water are oxidized by the OH radicals and the hydrogen peroxide. However, we have experimentally confirmed that the addition of hydrogen peroxide to a given solution had little effect on the hydrazine degradation. Therefore, it was considered that hydrazine was degraded by OH radicals.

It has reported that hydrazine is oxidized by O_2 and converted to nitrogen as below [14],



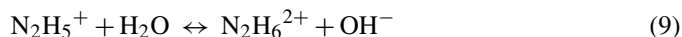
As OH radicals are stronger oxidizing agent than oxygen, it was thought that hydrazine and the ionic forms could be oxidized by OH radicals to form nitrogen. Therefore, it was suggested that the hydrazine and the ionic forms were degraded by OH radicals under ultrasonic irradiation condition as shown below,



It has been reported that the degradation rate of porphyrin increases with increasing rotation speed of the stirrer under ultrasonic irradiation condition [15]. In addition, it has been reported that the degradation rate of (4-chloro-2-methylphenoxy) acetic acid depends on dissolved gas species (nitrogen, air, oxygen and argon) under ultrasonic irradiation condition [16]. From these reports, the sonochemical degradation of hydrazine may be accelerated by mechanical stirring or optimum dissolved gas. A further experiment must be conducted to make it more clear.

4.2. Effect of pH on hydrazine degradation

Hydrazine is a weak base because the following dissociation reactions proceed in water.



The basic dissociation constants (K_{b1} and K_{b2}) of those are 8.5×10^{-7} and 8.9×10^{-16} , respectively. Fig. 5 shows the molar fraction of the equilibrium concentrations of nonionized hydrazine (N_2H_4), monovalent hydrazinium cation (N_2H_5^+) and divalent hydrazinium cation ($\text{N}_2\text{H}_6^{2+}$) as a function of pH, which were calculated by using the following relations, where the three regions in Fig. 4 are shown in Fig. 5.

$$[\text{N}_2\text{H}_5^+] = K_{b1} \frac{[\text{N}_2\text{H}_4]}{[\text{OH}^-]} \quad (10)$$

$$[\text{N}_2\text{H}_6^{2+}] = K_{b2} \frac{[\text{N}_2\text{H}_5^+]}{[\text{OH}^-]} \quad (11)$$

It was found that the $\text{N}_2\text{H}_6^{2+}$ concentration increases with the decrease in pH at a pH of less than 1, N_2H_5^+ becomes a predominant ionic species in the pH range of 1–6, and that of N_2H_4 increases with pH at a pH of more than 6. Furthermore, it is shown that $\text{N}_2\text{H}_6^{2+}$ increases with decreasing N_2H_5^+ in Region I, N_2H_4 increases with decreasing N_2H_5^+ in Region III, and the fraction of N_2H_5^+ is largest in Region II.

It is considered that hydrazine is degraded by OH radicals in Region I as shown in Eq. (7), in Region II as Eq. (6) and in Region III as Eq. (5), respectively. In Region I, the rate of hydrazine degradation increases with increasing the fraction of $\text{N}_2\text{H}_6^{2+}$

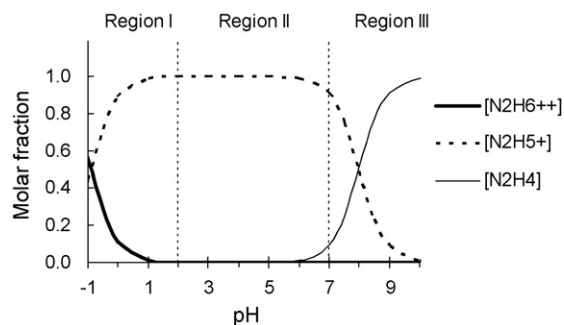


Fig. 5. The change in molar fraction of equilibrium concentration of N_2H_4 , N_2H_5^+ and $\text{N}_2\text{H}_6^{2+}$ as a function of pH. Each region corresponds to Fig. 4.

and in Region III, it increases with increasing the fraction of N_2H_4 . Therefore, it is suggested that N_2H_4 and $\text{N}_2\text{H}_6^{2+}$ are more easily degraded by OH radicals than N_2H_5^+ .

5. Conclusions

It was found that the hydrazine degradation took greatly place under the ultrasonic irradiation condition, but not under the stirring condition. This suggested that the hydrazine and the ionic forms are degraded by OH radicals. It was found that the rate of hydrazine degradation was largely dependent upon pH and divided into three regions. It was also estimated that the three regions were associated with the dissociating forms of hydrazine. It was assumed that hydrazine was more degraded at the dissociating form of N_2H_4 and $\text{N}_2\text{H}_6^{2+}$ than at that of N_2H_5^+ : Alkaline condition more than pH 7 and acidic condition less than pH 2 were efficient conditions for the hydrazine degradation under ultrasonic irradiation.

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