Decomposition of Nitogen Heterocyclic Compounds(NHCs) in Aqueous Solution by Sonication

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The sonolytic decomposition of NHCs, such as atrazine[6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine], simazine(6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine), trietazine(6-chloro-*N*,N,*N'*-triethyl-1,3,5-triazine-2,4-diamine), in water was investigated at a ultrasound frequency of 200kHz with an acoustic intensity of 200W under argon and air atmospheres. The concentration of NHCs decreased with irradiation, indicating pseudo-first-order kinetics. The rates were in the range 1.06~2.07 ($x10^{-3}$ min^{-1}) under air and 1.30~2.59($x10^{-3}$ min^{-1})under argon at a concentration of 200μM of NHCs. The rate of hydroxyl radicals(•OH) formation from water is 19.8μM min^{-1} under argon and 14.7μM min^{-1} under air in the same sonolysis conditions. The sonolysis of NHCs is effectively inhibited, but not completely, by the addition of *t*-BuOH(2-methyl-2-propanol), which is known to be an efficient •OH radical scavenger in aqueous sonolysis. This suggests that the main decomposition of NHCs proceeds via reaction with •OH radical; a thermal reaction also occurs, although its contribution is small. The addition of appropriate amounts of Fenton's reagent [Fe^{2+}] accelerates the decomposition. This is probably due to the regeneration of •OH radicals from hydrogen peroxide, which would be formed from recombination of •OH radicals and which may contribute a little to the decomposition.

Key words : Sonication, NHCs, Hydroxyl radicals, Fenton's reagent, Thermal reaction

1. Introduction 1

Irradiation by high power ultrasound in a liquid leads to the acoustic cavitation phenomenon, such as the formation, growth, and collapse of bubbles, accompanied by the generation of local high temperature, pressure, and reactive radical species. Thus, the acoustic cavitation in an aqueous solution results in chemical effects by the ultrasound [1-4]. It has been proposed that three different reaction sites in the cavitation bubble, i.e., the inside of the cavitation bubbles, the gas-liquid interfacial region of the cavitation bubbles, and the bulk solution are present during the ultrasonic irradiation [5,6].

In recent year, many researches on sonochemical decomposition of contaminants such as chlorobenzene [7], aliphatic aldehyde [8], chlorinated hydrocarbons[9,10], chlorofluorocarbon[11,12], volatile fatty acids[13], alkylphenol ethoxylate[14] in aqueous solution have been reported. The ultrasonic irradiation of aqueous systems could be an advantageous method to investigate the reactivity of hydroxyl radicals which play a significant role upon environmental chemistry as well as to investigate the thermal effects caused by ultrasound.

The wide utilization of pesticides for agriculture practices has already contributed to the increasing contamination of the environment. Among the different pollutants, NHCs such as atrazine, simazine and trietazine are priority pollutants to consider since they are widely used all over the world. The removal of such compounds at low levels from water always constitutes a problem. Among the methods employed are either destruction oxidation with ozone [15,16,17], hydrogen peroxide with different semiconductor suspensions assisted by light [18,19,20], adsorption into porous solids such as activated carbon, zeolites [21,22,23]. However the decomposition of these compounds by ultrasonic irradiation have not been reported. In this research, we report the results of sonochemical decomposition of NHCs.

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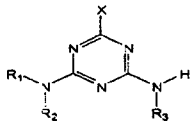
2. Experimental Methods

2.1 Materials

Reagent grade atrazine, simazine and trietazine (c.f., Fig.1) were purchased from Wako and used without further purification. Argon of five-nine grade was purchased from Osaka Sanso, and all solutions for the experiment were prepared with water purified by a Millipore Milli-Q system (R= 18.2 MΩ · cm).



Trivial name	X	R1	R2	R3
Atrazine	Cl	CH_3CH_2	H	$CH(CH_3)_2$
Simazine	Cl	CH_3CH_2	H	CH_3CH_2
Trietazine	Cl	CH_3CH_2	CH_3CH_2	CH_3CH_2

Fig. 1. Chemical structure of used NHCs.

2.2 Ultrasonic irradiation

Fig.2 shows the ultrasound irradiation set-up. The ultrasonic reactions were performed using a Kaijo Denki multi-wave ultrasonic generator Model 4021, and a 65 mm diameter barium titanate oscillator, operated at 200kHz, with an input power of 200W(6W/cm^2). The reaction cell was immersed into the water bath, cooled by an external cooler to keep the temperature constant at 25℃. The cylindrical vessel(150ml) had a side arm with a septum for gas bubbling or/and for extracting the gaseous and liquid samples. The bottom thickness of the vessel was approximately 1.0 mm for good transmission of the acoustic waves during the ultrasonic irradiation. The vessel was mounted at a constant position from the oscillator relative to a nodal plane of the sound wave (3.8 mm: half a length of the ultrasound wave). During the irradiation, the vessel was sealed and sonicated to desired time intervals.

2.3 Identification and determination

Atrazine, simazine and trietazine were analyzed by using a HPLC(Shimadzu LC-6A) equipped with a UV photodetector and an ODS-18 column (6 x 150mm). A mixture of 100mM $NaClO_4$ and CH_3CN(50:50) was used as the eluent with a flow rate of 1.0ml/min. CO, CO_2 and methane were determined using a GC (Hewlett-Packard 6890) equipped with a thermal conductivity detector, and all the experiments were made in duplicate and the results presented in the paper are the average of two experiment.

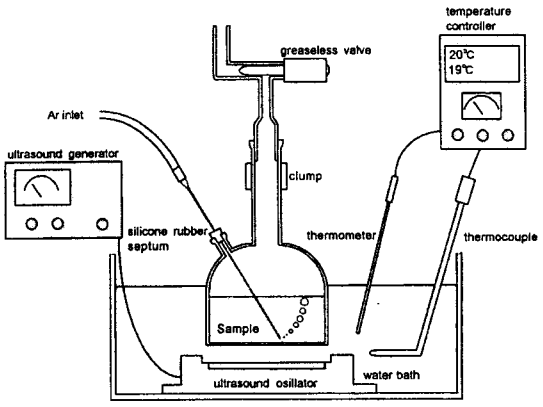


Fig. 2. Schematic description of the ultrasonic irradiation vessel.

3. Results and Discussion

Fig.3 shows the change in concentration as a function of time during the decomposition of NHCs by ultrasonic irradiation. The initial concentration of all the solutes was 200μM. The pseudo-first-order rate constants for NHCs decomposition under the conditions of the present work, kt is defined in *eq*(1) as

$$\ln(C/C_0) = -kt \quad \text{---------- (1)}$$

Where C is the NHCs concentration at time t, C_0 is the initial NHCs concentration, and k is the apparent pseudo-first-order rate constansts. The apparent rate constants k was calculated from *eq*(1), these results are presented in Table 1. The degradation rates(10^{-2}min^{-1}) of these solutes under an atmosphere of argon/air followed the order atrazine(2.59/2,07) > trietazine(2.23/1.65) > simazine (1.30/1.06). The decomposition rates of NHCs under argon were faster than that under air. During the sonolysis of an aqueous solute solution, the dependence of nature of the saturating gas, such as the solubility in water and the thermal

conductivity was observed in the same manner as our previous studies[24,25].

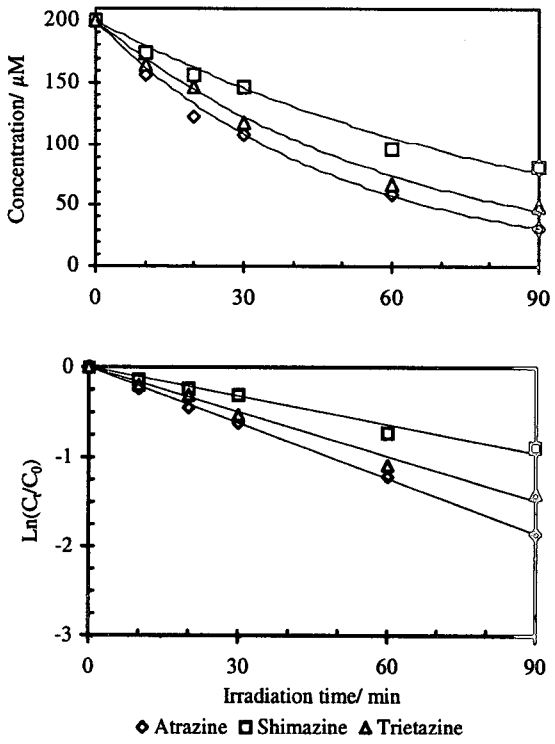


Fig. 3. Change of concentration as a function of the time during the decomposition of NHCs by sonication under air. The dots represent the logarithm of ratio between actual(C_t) and initial (C_0) concentration.

This implied that the maximum temperature in side the cavitation bubble, when acoustic cavitation bubbles were violently collapsed, depends on the ratio of the specific heat ratio ($r = C_p/C_v$) and the thermal conductivity of the saturating gas. In addition, the formation of reactive radical species(•OH, •OOH) would be enhanced because of the high temperature inside the collapsing cavitation bubble. Table2 indicates the decomposition rates of NHCs in aqueous solution saturated with various gases. The order of the decomposition rate is as follows; argon> nitrogen ≥ air. Specific heat ratio of the envelope gas used are Table2, and results show that the decomposition rate was increased with increasing r value of the envelope gas. Fig.4 shows a pH change of the sample solution during sonication of atrazine under air.

The pH dropped from its initial value of 12.5 to 5.2 at the end of run. It is known that nitrate and/or nitrite anion are produced during a sonication of aqueous solution under air atmosphere and thus, the pH of the aqueous solution usually decreases with sonication time under air atmosphere. In order to examine the effect of pH on decomposition of NHCs by irradiation ultrasound, the decomposition rate of NHCs in buffer solution was measured at various pH ranging from 4.3 to 11. As shown in Fig. 5, the rate in creased slightly with decreasing pH of the sample solution.

To Enhance the decomposition efficiency, a more effective utilization of •OH radical is desirable. It is expected that Fe^{2+} ions will regenerate •OH radicals from H_2O_2, thus the efficeiency of ultrasonic decomposition of atrazine will increase by presence of an appropriate concentration of Fe^{2+} ions.

Table 1. Results of kinetic data for decomposition of NHCs by sonication

NHCs	k^a		kOH^b
	in air	in argon	
Atrazine	2.07	2.59	4.7
Trietazine	1.65	2.23	3.6
Simazine	1.06	1.30	1.7

a Pseudo-First-Order rate constants ($10^{-2}min^{-1}$)
b Rate constants of hydroxyl radical(k_{OH}) reaction ($M^{-1}s^{-1}$)

Table 2. Results of kinetic data for decomposition of NHCs by sonication

Atmosphere	k^a	*Cp/Cv (1atm 300k)*[b]
Argon	2.59± 0.27	1.670
Oxygen	-	1.369
Air	2.07± 0.21	1.402
Nitrogen	1.96± 0.19	1.401

a Decomposition rate constants (10^{-2} min^{-1})
b J.Hilsenrth et al.,"*Table of Thermal Properties of Gases*", NBS Circular, 564(1995).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \cdot OH \text{ -- (2)}$$
$$\cdot OH + NHCs \rightarrow \text{decomposition -------- (3)}$$
$$\cdot OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \text{---------- (4)}$$

Fig.6 show the effect of Fe^{2+} ions on the decomposition of atrazine. The decomposition of atrazine was enhanced in the presence of Fe^{2+}: the rate increased to 2.1 times($4.33x10^{-2}min^{-1}$) at 1.0mM of Fe^{2+} concentration and to 1.6 times ($2.69x10^{-2}min^{-1}$) at 2.0mM. The results suggest that there is an optimum Fe^{2+} concentration for atrazine decomposition with maximal efficiency and that an excessive amount of Fe^{2+} leads to a decrease in the decomposition rate due to the scavenging of · OH radicals by Fe^{2+} ions as in *eq.*(4).

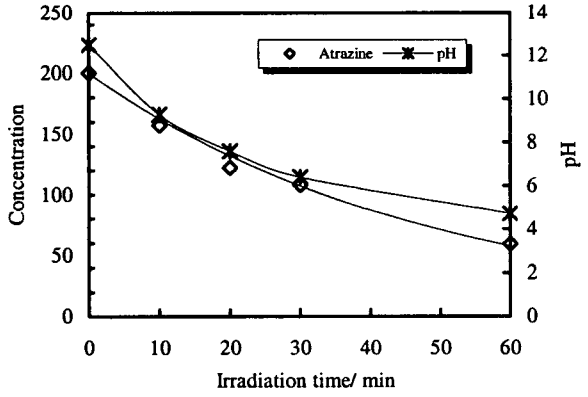


Fig. 4. Change in atrazine concentration and pH versus sonication time under air.
[Atrazine]$_i$ = 200μM, initial pH= 12.5.

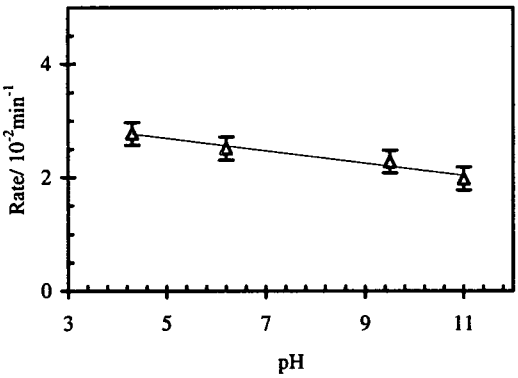


Fig. 5. Effect of pH on the decomposition rate of atrazine by sonication under air.

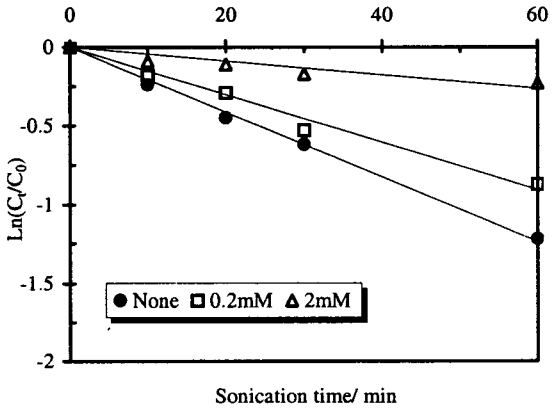


Fig. 6. Effect of Fe^{2+} on the decomposition of atrazine by sonication under air.

The contribution of the radical reaction by •OH

radicals was examined by addition of *t*-BuOH, which is known as an effective ·OH radical scavenger, into the sample solution. Result is indicated in Fig.7. The decomposition of atrazine was suppressed about 78% by the *t*-BuOH addition. This result suggests that decomposition of about 78% proceeds via radical reaction and that of about 28% via thermal reaction in sonochemical decomposition of NHCs in water at the present experimental conditions.

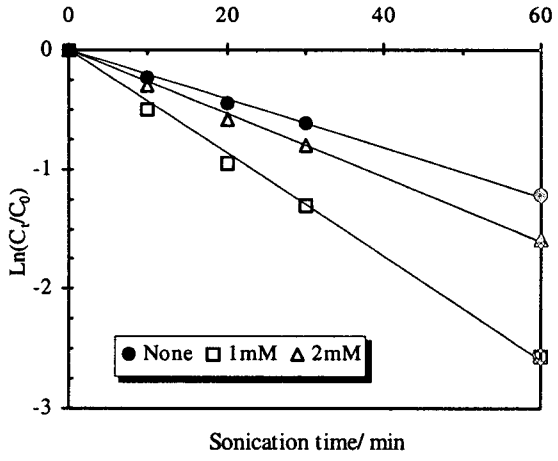


Fig. 7. Effect of *t*-BuOH addition on the decomposition of atrazine by sonication under air.

4. Conclusions

The decomposition system using ultrasound irradiation processes was applied to the decomposition of typical nitrogen heterocyclic compounds (NHCs) such as atrazine, simazine and trietazine The main results are summarized as follows:

First, this treatment method of ultrasound irradiation is very simple and comfortable for decomposition of NHCs to compare to other treatments have developed.

Second, this treatment has ability to decomposition for NHCs over 50~75% in short treatment time. Also it is very particle method for the price that is very cheap to operate.

Finally, this treatment has high possibility for decomposition NHCs, so that it can be expected highly as a new treatment method in near future.

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