

Sonochemical Destruction of Aliphatic Aldehydes in an Aqueous Solution

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수용액중 초음파조사에 의한 Aldehyde류의 초음파분해

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국문요약

Propionaldehyde, n-Butyraldehyde, n-Valeraldehyde 수용액에 주파수 200 kHz, 출력 6.0W/cm²의 초음파조사(超音波照射)후 그 분해반응에 관해 고찰했다. Aldehyde류는 초음파 조사에 의해 빠르게 분해되었고, 분해형태는 유사1차 반응을 나타내었다. 이들의 분해 속도는 Propionaldehyde < n-Butyraldehyde < n-Valeraldehyde의 순서에 따랐다. 초음파 조사시 아르곤 등의 포화가스(Envelope gas)의 영향은 큰 것으로 나타났고 순수한 아르곤 분위기에서 Aldehyde류의 분해 속도(K_{obs})는 1.6 × 10⁻³ min⁻¹ ~ 3.3 × 10⁻³ min⁻¹ 으로 공기 분위기에서의 분해 속도(K_{air}) 9.3 × 10⁻³ min⁻¹ ~ 2.1 × 10⁻² min⁻¹ 보다 빠르게 나타났다. 초음파분해에 의한 분해생성물로 기상(Gas phase)중에서는 CO, CO₂ 및 CH₄, 그리고 액상(Liquid phase)중에서는 미량의 저급 유기산(HCOO, CH₃COO)이 검출되었다.

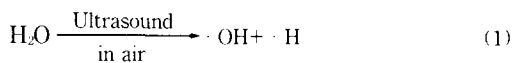
Key words: Aliphatic aldehydes, Ultrasound, Cavitation, Destruction

I. Introduction

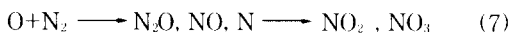
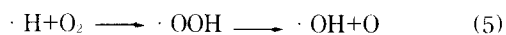
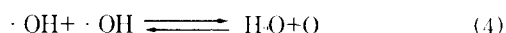
The ultrasonic cavitation is a phenomenon of bubble nucleation, growth, and violent adiabatic collapse, which can lead to localized temperatures as high as several thousand K and pressures a few hundred atmospheres^{1,2)}. These levels of temperatures and pressures lead to free radical formation and are believed to be responsible for most of the chemical effects of ultrasonic energy. Therefore, the ultrasonic irradiation is a powerful physical method of affecting many chemical reaction and the impacts of ultrasound on chemical reactions are many sites in its effects due to the influence of one or more factors on the kinetics, mechanism or even the direction

of chemical process. The ultrasonic energy is absorbed by the material and is converted to heat. Internal heating is caused by hysteresis and molecular absorption, and surface heating results from the friction between particles. Although the increase of bulk temperature is not significant at low intensity levels, a localized temperature increase at the interface between a solid and a liquid can significantly decrease the surface tension and viscosity. The chemical effects of ultrasound have been explained in terms of reactions occurring in side, at the interface, or at some distance away from cavitating gas bubbles.

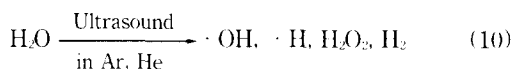
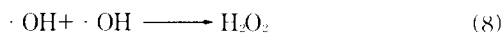
As principal products, in the case of water saturated with air, the first step appears to be the cleavage of water and the molecular oxygen.^{3,4)}



Inside the bubble or in the liquid shell surrounding the cavity, these radicals can combine in various ways or react with gases and vapor present, leading to the detection in the medium of HNO_3 , HNO_2 , and H_2O_2 .³⁾



The main fraction of the H_2O_2 formed during water sonolysis seems to come from the $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals, which combine in the bubble or/and in the layer surrounding the bubble of cavitation in the absence of substrate⁶⁾ (reactions 8, 9).



In recent years, the sonochemical destruction of a variety of chemical contaminants in aqueous solution has been previously reported.^{7,12)} The substrates are transformed into short chain organic acids, CH_4 , CO_2 , and inorganic ions as the final products.

Aliphatic aldehydes such as propionaldehyde (PA), n-Butyraldehyde (BA) and n-Valeraldehyde (VA) with unpleasant suffocating odors have low odor threshold and have become recognized world-wide as problem of treatment for industrial waste water and odor pollution of air. Removing these compounds, adsorption methods using activated carbon^{14,1)}, oxidation by ozone^{15,16)} have been investigated. However, the destruction and deodorization of aldehydes by sonication almost have not been reported.

In this study, we report the results of sonolysis and deodorization of aliphatic aldehydes by ul-

trasonic irradiation, and also discuss the mechanism of destruction.

II. Materials and Methods

1. Materials

Propionaldehyde, n-Butyraldehyde, n-Valeraldehyde and tert-Butyl alcohol (tert-BuOH) were used as received from Wako Pure Chemical Industries Co. Inc. All chemicals were of at least 99% purity and were used without further purification. Bubbling gas (argon) of four-nine grade was purchased from Osaka Sanso, and solutions of aldehyde were made with water purified by a Millipore system (MILLI-Q Labo).

2. Apparatus and Procedures

Fig. 1 shows the apparatus used for the sonication of substrate in the present study. A multiwave ultrasonic generator (KAJJO 4021) and a barium titanate oscillator of 65 mm ϕ (were used for ultrasonic irradiation and operated at 200 kHz with an input intensity of 200W. A cylindrical

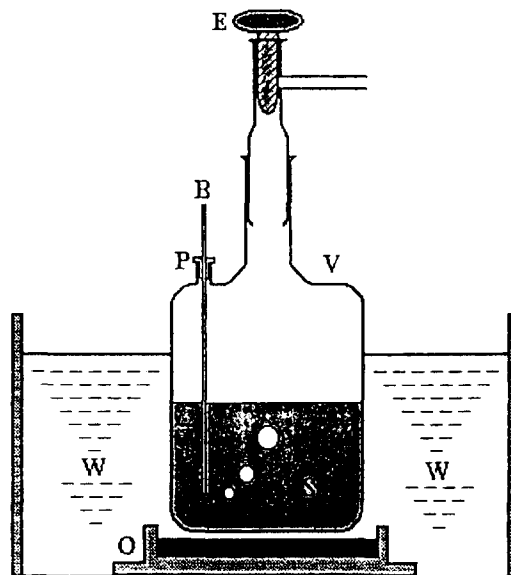


Fig. 1. Schematic diagram of the ultrasonic irradiation vessel. Gas (solute) inlet and outlet; B, sample solution; S, glass vessel; V, silicon septum; P, cock or stopper (close during irradiation); E, cooling water; W, oscillator; O

glass vessel of 65 mm ϕ with total volume of 150 ml was used for ultrasonic irradiation. The vessel has a side arm with a silicon rubber septum for gas bubbling, substrate injection or sample extraction, and the vessel was fitted at a constant position of a nodal plane of the ultrasound wave ($\lambda/2$; 3.8 mm upon the oscillator). During the irradiation the glass vessel was sealed. The water (60 ml) was bubbled by argon for 30 minutes (flow rate 0.3 l min⁻¹), substrate was injected before irradiation. The irradiation was stopped at desired time intervals, and the solution (2.0 ml) was extracted in a sealed bottle (5.0 ml) by a glass syringe (10 ml) for analysis.

The initial gaseous odor sample was prepared by the dilution of irradiated solution (20 μ l) in a vacuum glass bottle (1.0 l) for odor sensory measurements, and it was diluted with high purity helium to the threshold odor number by the triangle plastic bag (3.0 l) method, i.e., it is a sort of odor sensory measurements, that is, a method that six panellers guess which is the odor-containing bag among three plastic bags: Only one of three bags is odor-contained air and the others are odorless air.

3. Analysis

The concentration of substrate was determined by a gas chromatography (Hewlett-Packard 5890 GC/FID) with a 15 m \times 0.3 mm i.d. \times 0.33 μ m film thickness DB Ultra-1 capillary column. The determination of products (organic acids) was performed by an ion chromatography analyzer (IC-100), and gases such as carbon dioxide, carbon monoxide and methane were determined by a gas chromatography (Hewlett-Packard 5890 GC/TCD) with a molecular sieves (30/60 mesh) 3.0 mm i.d. \times 2.0 m stainless-steel column for carbon monoxide, a Porapak Q (30/60 mesh) 2.0 mm i.d. \times 2.0 m stainless-steel column for carbon dioxide and methane. Total organic carbon (TOC) was measured by a total organic carbon analyzer (Shimadzu TC-500).

III. Results and Discussion

1. Destruction of aldehydes

Fig. 2 shows the concentration vs irradiation time-profiles for Propionaldehyde, n-Butyraldehyde, and

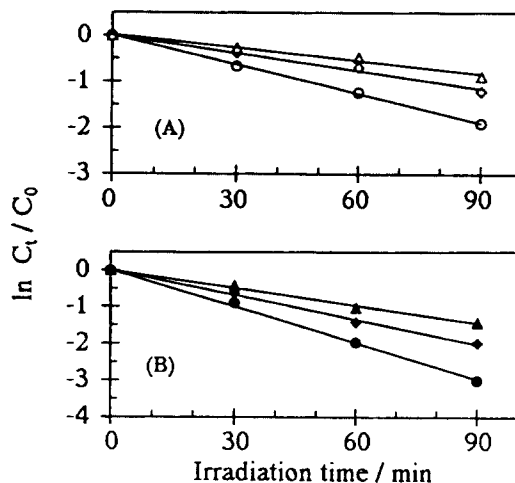


Fig. 2. Destruction of aldehydes by ultrasonic irradiation. Initial concentrations (C_0) for VA, BA and PA were 1.02, 1.03 and 1.01 mM, respectively.

(A) under air, \circ : VA, \diamond : BA, \triangle : PA
(B) under argon, \bullet : VA, \blacklozenge : BA, \blacktriangle : PA

n-Valeraldehyde. The concentration of aldehydes decreased exponentially with irradiation time. In the presence of pure argon atmosphere, the pseudo-first-order destruction rate constants of $k_{PA}=1.6 \times 10^2$ mM min⁻¹, $k_{BA}=2.3 \times 10^2$ mM min⁻¹, $k_{VA}=3.3 \times 10^2$ mM min⁻¹ and in the presence of air atmosphere, the rate constants of $k_{PA}=9.3 \times 10^3$ mM min⁻¹, $k_{BA}=1.5 \times 10^4$ mM min⁻¹, $k_{VA}=2.1 \times 10^2$ mM min⁻¹ were determined from the slopes of initial decay curves. The decay rates in the argon-saturated solution are faster than those in the air atmosphere, as shown in Table 1 and 2. These results suggested that ther-

Table 1. Results of kinetic data for destruction of aldehydes by sonication

Solute	P_{VAP}^a	R^b	k^c	
			under Argon	under Air
Propionaldehyde	318.1	2	1.6	0.9
n-Butyraldehyde	112.1	3	2.3	1.5
n-Valeraldehyde	34.3	4	3.3	2.1

^aVapor pressure (mmHg) was calculated by Antoine's equation at 25°C. "Kagaku Binran". The Chemical Society of Japan, 1975.

^bHydrophobicity R , A. Henglein, and C. Kormann, J. Radiat. Biol., 48, 251, 1985.

^cPseudo-first-order rate constant ($10^2 \cdot \text{min}^{-1}$).

Table 2. Sonochemical destruction rates of aldehydes with OH_{rate} and C_p/C_v of atmospheric gases

Division	Rate constant	
	under Argon	under Air
Propionaldehyde	1.6	0.9
Butyraldehyde	2.3	1.5
n-Valeraldehyde	3.3	2.1
OH_{rate}	20.0	≥ 15
C_p/C_v	1.67	1.40

^aPseudo-first-order rate constant ($10^{-2} \cdot \text{min}^{-1}$).

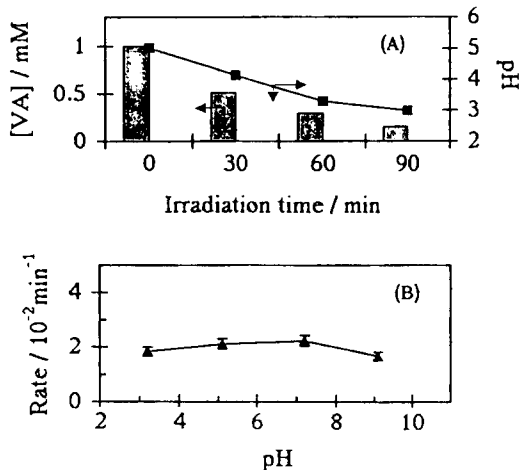
^bFormation rate ($\mu\text{M} \cdot \text{min}^{-1}$) of OH radical in our experimental conditions. Y. Nagata *et al.*, Decomposition of Hydroxybenzoic Acids in water by Ultrasonic Irradiation. Environ. Sci. Technol., 30, 1133, 1996.

^cSpecific heat ratio. J.Hilsenrath *et al.*, "Tables of Thermal Properties of Gases", NBS circular, 564, 1955. At 1atm, 300K.

mal conductivities ($\gamma=C_p/C_v$) of the dissolved gases have been inversely correlated to sonochemistry field²¹ as well as to variable rates of free-radical formation during sonolysis. It is known that the efficiency of acoustic cavitation is dependent upon the dissolved gas, therefore, the rate of destruction would be faster under pure argon than under air atmosphere.

2. Effect of pH of aqueous solution

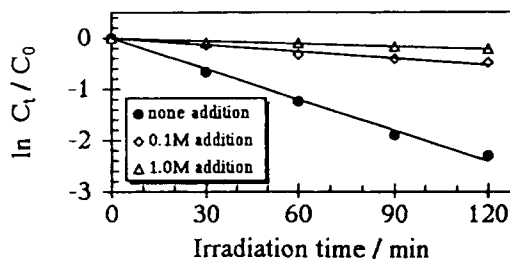
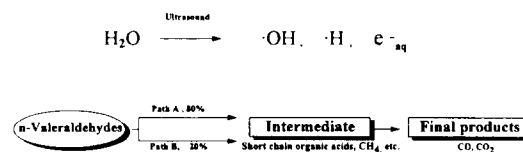
Fig. 3A shows a pH change of the sample solution during sonication of n-Valeraldehyde under

**Fig. 3.** Change in VA concentration and pH versus irradiation time by sonication under air.

air atmosphere. The pH of aqueous solution dropped from its initial value of 5.0 to 2.9 at the end of run. It is known that NO_2 and/or NO_3 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. Over a pH range of 3.2 to 9.1, the destruction rate constants are essentially invariable in a sonicated solution as shown in Fig. 3B. This pH dependency is consistent with the tendency for water in a dense supercritical state to have a higher ion activity product relative to normal phase water.

3. Scavenging effect of OH radicals

The chemical effects of tert-BuOH are investigated to the sonochemistry field as a scavenger of hydroxy radicals by Henglein and co-workers.²⁰ There was found that the scavenging efficiency could be related to the hydrophobicity of the solutes, and this was taken as an indication that the scavengers reacted with the hydroxy radicals in an interfacial region at the bubbles where the solutes were accumulated. Fig. 4 shows the effect of scavenging by tert-BuOH on the destruction of n-Valeraldehyde under air. The destruction was not completely suppressed by tert-

**Fig. 4.** Destruction of VA as a function of t-BuOH addition to aqueous solution under air.**Fig. 5.** Destruction pathway of n-Valeraldehyde by sonication. Path A: Free radical reaction. Path B: Combustion

BuOH addition, i.e., it was suppressed about 80% and this result suggests that the destruction reaction is not only thermalolysis took place in the interfacial area but also it is radical reaction in bulk liquid phase, i.e., the result indicate that the destruction of about 80% proceeds via radical reaction in interfacial region initiated by hydroxy radical and that of about 20% thermal reaction in cavities. The destruction pathway of *n*-Valeraldehyde was shown in Fig. 5.

4. Relation between products and reactants destruction

Fig. 6 and 7 shows the relationship of total organic carbon, product formation and time-profiles of *n*-Valeraldehyde by ultrasonic irradiation under argon. The concentration of solute is completely cleaved after 150 minutes sonication. However, even if the total amount of organic carbon was not decreased, i.e., it was cleaved about 40 % of initial total organic carbon, the decrease amounts of total organic carbon were agreed with a total amount of products as carbon dioxide, carbon monoxide and methane at the gas phase, and this

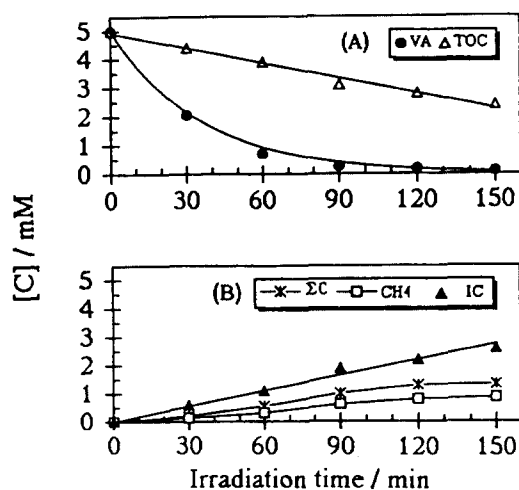


Fig. 6. Relation between formation of products and VA destruction by sonication under argon. (A) relationship of TOC and VA concentration. (B) relationship of IC, CO_2 , CO and CH_4 . VA concentration was calculated as carbon concentration. ΣC is the total amount of CO_2 and CO, and IC is a difference between initial TOC and TOC.

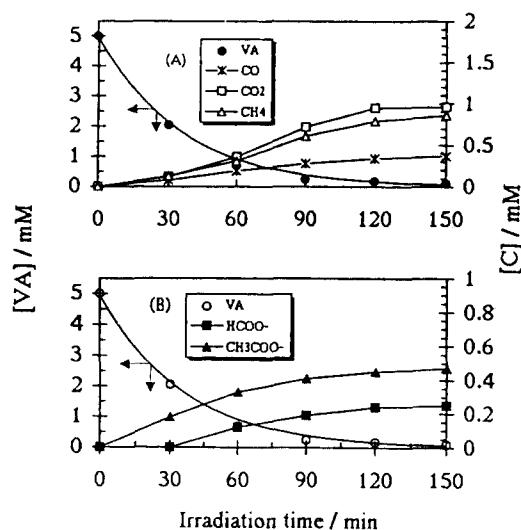


Fig. 7. Time-profiles of destruction of VA and formation of products by ultrasonic irradiation under argon. VA concentration was calculated as carbon concentration. (A) in gas phase, (B) in liquid phase

result suggested that a number of destroyed *n*-Valeraldehyde take part into the formation of short-chain aliphatic organic acids forms as formic acid, acetic acid, etc. in aqueous phase.

5. Change of odor intensity by sonication

The deodorization is also conducted by triangle plastic bag method for odor sensory measurement in sonolysis of *n*-Valeraldehyde under air atmosphere. Fig. 8 shows how the odor in-

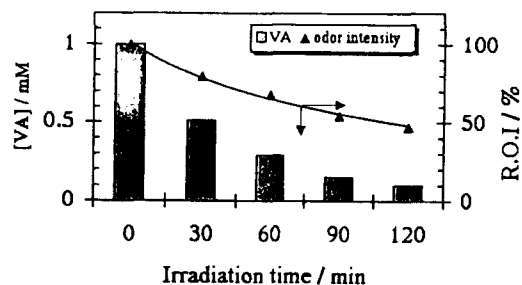


Fig. 8. Relation between odor intensity and destruction of VA by ultrasonic irradiation under air. Relative odor intensity (ROI) is the difference between initial odor intensity and odor intensity by sensory measurement method.

tensity varied with irradiation time, and it indicated that over 50% of the initial odor intensity was deodorized with destruction by the sonication.

Finally, from the results on variation of an our experimental parameter of sonolysis, we conclude that the destruction for aliphatic aldehydes under ultrasonic irradiation in water can be expected by following observation:

(1) The order of the destruction rate is as follows: Propionaldehyde < n-Butyraldehyde < n-Valeraldehyde, i.e. the rate is increased with the increment of hydrophobicity, vapor pressure of solutes, and it's also increased with the increment of hydroxy radical formation rate, specific heat ratio (C_p/C_v) of saturating gas in aqueous solution.

(2) The aldehydes were destructed by both the reaction of free-radical attack in the bulk liquid phase and pyrolysis in the cavitation bubble or interfacial region of bulk solution.

(3) The simplicity and flexibility along with the high efficiency of destruction indicate the potential of a sonochemical-based process to become a competitive technology with other advanced water treatment technologies.

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