Acoustic Cavitation in Water under Rare Gas Atmosphere

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The results of the sonolysis of water and aqueous 2-methyl-2-propanol under a rare gas atmosphere suggest that increasing the solubility of the rare gas in water significantly enhances the rate of sonolysis but their thermal conductivity does not significantly affect the temperature of the cavitation bubbles.

The chemical effect of ultrasounds is thought to be attributed to acoustic cavitation; the formation, growth and instantaneous collapse of micro bubbles in a liquid. Various physical and thermodynamic properties of an ultrasound-exposed liquid and surrounding gas would influence the cavitation efficiency.[1] In the sonochemical reaction, a rare gas is often used as the surrounding gas due to its high polytropic index ($C_p/C_v = 1.67$) and chemical inertness. A high C_p/C_v value will produce a higher temperature and give a high reaction yield. There have been some investigations on the dependence of rare gases on cavitation and it was reported that the effectiveness of the gases on the rate of reaction, the temperature of the bubble interior and intensity of the sonoluminescence was in the order Xe > Kr > Ar > Ne > He in every case. However, studies related to the quantitative comparison of the cavitation effect among rare gases are still limited.

In this paper, the sonolysis of water and aqueous 2-methyl-2-propanol (*t*-BuOH) is carried out under an atmosphere of five rare gases, and the reaction efficiency is evaluated based on the degradation rates and the temperature inside the cavitation bubbles (hereafter defined as the cavitation temperature) is estimated from the distribution of the sonolysis products. Since ultrasounds have become a promising tool for synthetic chemistry and waste degradation,[2] the investigations about cavitation from various view points are important for obtaining the optimum reaction conditions as well as fundamental data.

The sonolysis experimental procedure was almost the same as those previously reported.[3] In short, a rare gas-saturated water or aqueous *t*-BuOH solution was sonicated in a cylindrical glass vessel. The vessel had a side arm with a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The bottom of the vessel was flat and made as thin as possible (1 mm) because the transmission of the ultrasonic waves increases with decreasing thickness of the bottom. The vessel was mounted at a fixed position relative to the nodal plane of the sound wave (3.75 mm: $\lambda/2$ from the oscillator). A multiwave ultrasonic generator and a barium titanate oscillator were used for the ultrasonic irradiation and operated at 200 kHz with an input intensity of 200 W. To fix the reaction vessel at an exact position, a laboratory jack, clamp and holder–all the parts used for the positioning system in optical measurements–were used. During the irradiation, the vessel was closed. Under these conditions, the temperature rise of the solution was ca. 7 °C after a 10 min sonication.

Hydrogen, oxygen, acetylene, ethylene and ethane were determined by a gas chromatograph. Hydrogen peroxide was determined from the amount of Fe(III) formed by the H_2O_2-oxidation of Fe(II).[4]
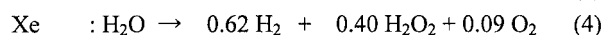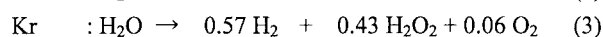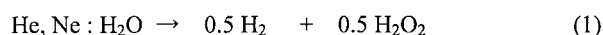
Table 1. Sonolysis of water in different rare gases

Gas	Rate of Formation / μM min⁻¹				H/O in Products
	R(H₂)	R(H₂O₂)	R(O₂)	-R(H₂O)[b]	
He	–[a]	1.9	trace	3.8	
Ne	–[a]	2.8	trace	5.6	
Ar	12.3	10.6	0.94	23.0	1.99
Kr	20.9	15.8	2.36	36.5	2.03
Xe	27.2	17.8	3.82	44.1	2.08

[a]Cannot be determined due to the overlapping retention times of H_2 and He (Ne). [b]Estimated from $-R(H_2O) = [R(H)/2 + R(O)]/2$, $R(H) = 2R(H_2) + 2R(H_2O_2)$, $R(O) = 2R(H_2O_2) + 2R(O_2)$.
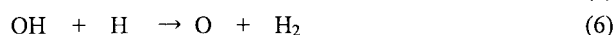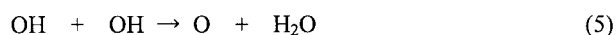
The sonolysis mode of water under different rare gases is shown in Table 1. The amount of reaction products from the water sonolysis were proportional to the sonication time at the initial time (over 10 min) and the rates of formation of product were in the order Xe > Kr > Ar > Ne > He with significant difference. This order was consistent with the results of the OH radical formation (by spin trapping measurement),[5] H_2O_2 (KI method) and OH radical formations (fluorescence from terephtalic acid),[6] H_2O_2 formation (titanyl sulfate method),[7] and sonoluminescence studies.[8]

The degradation products were hydrogen, hydrogen peroxide and oxygen. No other products were detected. The fact that the H/O ratio of the products under Ar, Kr and Xe were nearly equal to 2 indicates that the experimental results are reliable.

The degradation of water would proceed with the following stoichiometry:[9]

$$\text{He, Ne}: H_2O \rightarrow 0.5\,H_2 + 0.5\,H_2O_2 \qquad (1)$$

$$\text{Ar} \quad : H_2O \rightarrow 0.53\,H_2 + 0.46\,H_2O_2 + 0.04\,O_2 \quad (2)$$

$$\text{Kr} \quad : H_2O \rightarrow 0.57\,H_2 + 0.43\,H_2O_2 + 0.06\,O_2 \quad (3)$$

$$\text{Xe} \quad : H_2O \rightarrow 0.62\,H_2 + 0.40\,H_2O_2 + 0.09\,O_2 \quad (4)$$

Oxygen may be formed via eqs. 5 –7.

$$OH + OH \rightarrow O + H_2O \qquad (5)$$

$$OH + H \rightarrow O + H_2 \qquad (6)$$

$$O + O \rightarrow O_2 \qquad (7)$$

Eqs. 5 and 6 would occur under high temperature conditions,[10] therefore, it is postulated that the cavitation temperature increased in the order Xe > Kr > Ar > Ne, He, that is, the same order of increasing oxygen yield, but the degree of its variation was not as significant as that observed for the rate of sonolysis of water.

Table 2. Sonolysis of *t*-BuOH

Gas	-R(*t*-BuOH) /μM min^{-1}	Ratio^a	Cavitation Temp. / K	T.C^b /10^{-4}W m^{-1}K^{-1}	Solubility^c / cm^3 kg^{-1}
He	1.5	8.7-13.1	3350-3650	1510	0.86
Ne	2.9	8.0-14.0	3300-3700	493	10.5
Ar	4.5	9.6-14.4	3400-3700	179	33.6
Kr	5.9	9.8-14.4	3450-3700	94.2	59.4
Xe	9.5	9.7-15.7	3450-3800	56.2	108

^{a}(C$_2$H$_4$ +C$_2$H$_2$)/C$_2$H$_6$. ^{b}Thermal conductivity. ^{c}Solubility of rare gas in water.

Table 2 shows the sonolysis data of the aqueous *t*-BuOH solution at concentrations of 0.1, 0.5, 1, 2.5, 5 and 10 mmol/L. The order of the rate of *t*-BuOH degradation was same as the rate of water degradation.

During the sonolysis of volatile organic substances, ethane, ethylene and acetylene are formed along with other pyrolysis products. The cavitation temperature can be estimated from the ratio [R(C$_2$H$_4$) + R(C$_2$H$_2$)] / R(C$_2$H$_6$).[11–13] The ratio and estimated temperature are shown in Table 2.[14] The temperature under argon was in good accord with the reported value of aqueous *t*-BuOH sonolysis under argon (3600K)[13] but somewhat lower than that estimated from the sonoluminescence experiments in dilute aqueous benzene (4300K).[15]

It is considered at this time that the extent of the cavitation effects depends on the thermal conductivity of the gas; the greater the conductivity of the gas, the more heat is dissipated to the surroundings, effectively decreasing the cavitation temperature. In fact, the cavitation temperatures estimated from the multi bubble sonoluminescence from Cr(CO)$_6$ in octanol were reported to be Xe (5100K) > Kr (4400K) > Ar (4300K) > Ne (4100K) > He (3800K) which is the same order of decreasing thermal conductivity.[16] However, our results exhibited somewhat different features from these results. In both cases for the sonolysis of water and *t*-BuOH, the degradation rates were Xe > Kr > Ar > Ne > He with a significant difference. On the other hand, the cavitation temperature is in the same order but the difference is small, that is, the thermal conductivity of the gas does not appreciably affect the cavitation temperature.

As another factor for the effect of cavitation, the solubility of the rare gas in water attracted our attention. The rate of sonolysis of water and *t*-BuOH increased with the increasing solubility (Table 2). A similar trend in solubility dependence was reported[7] for the H$_2$O$_2$ formation from water sonolysis under Ar and N$_2$ atmospheres.

The present results suggest that increasing solubility leads to a larger number of cavitation nuclei and an enlarged chance of chemical reaction, and that the collapse of the bubbles is so rapid that it proceeds nearly adiabatically, therefore, the difference in the thermal conductivity of the different gases is not very significant. However, it may be premature to draw any conclusions from the results of only the *t*-BuOH sonolysis. The effects of various conditions such as frequency and intensity of ultrasound and solvent and solute should be considered and additional accumulation of pyrolysis data from the sonolysis of volatile organic compounds is required for a detailed discussion of the cavitation temperature based on the chemical reaction.

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14 The ratio equals the ratio k_1/k_2, k_1 (rate constant for $2CH_3 \rightarrow C_2H_6$) = 2.4 × 10^{14}T$^{-0.4}$dm^3 mol^{-1}s^{-1}, k_2 (rate constant for $2CH_3 \rightarrow C_2H_4 + H_2$) =1.0 × 10^{16}exp(−134kJ/RT) dm^{3}mol^{-1}s^{-1}
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