Ultrasonic Enhancement on the Hydrolysis of Diethyl 1,2-Benzenedicarboxylate

Bongbeen Yim,* Youngeok Yoo,[†] Yoshio Nagata, and Yasuaki Maeda
Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531
[†]*College of Education, Taegu University, Kyungsan-city, Kyungpook 712-714, Korea*

(Received June 18, 2001; CL-010572)

The ultrasonic enhancement on the hydrolysis of diethyl 1,2-benzenedicarboxylate results from the dissipated heat when the cavitation micro-bubbles were vigorously collapsed. The effective temperature in a solution depends on the nature of the dissolved gas. The relatively broad region that spreads from the interface of the cavitation micro-bubble plays an important role in the sonolytic hydrolysis of esters.

Sonication of an aqueous solution leads to a process called cavitation, which is the formation, growth, and adiabatic collapse of the micro-bubbles. The temperature and pressure derived from the violent collapse of the cavitation micro-bubbles are estimated to be up to 5000 K and 1000 bar, respectively. Reactive free radicals in aqueous solution are generated under these extreme conditions.[1] The sonochemical effects are the result of the cavitation phenomenon.

The hydrolysis of esters such as methyl acetate,[2] carboxylic acid esters,[3] and nitrophenyl esters[4] by sonication has been reported, but the description with respect to the sonochemical effect is limited. It was recently reported that the formation of transient supercritical water was an important factor in the acceleration of the sonolytic hydrolysis.[5] However, the formation and role of supercritical water for the hydrolysis in the presence of ultrasounds are still uncertain.[6]

In this paper, we report the ultrasonic enhancement on the hydrolysis of aqueous diethyl 1,2-benzenedicarboxylate solutions under homogeneous conditions. The formation rate of monoethyl 1,2-benzenedicarboxylate regarded as the product of hydrolysis was determined. In order to investigate the chemical effect induced by sonication, sonications under an atmosphere of five dissolved gases were also carried out.

All the reagent grade chemicals were purchased from Wako. The water used for the experiments was purified by a Millipore Milli-Q system. Before sonication, the sample solution was prepared by bubbling a high purity gas (> 99.99%), and the pH was adjusted with phosphate buffer and sodium hydroxide solution. For the purpose of sonication, the experimental apparatus consisted of an ultrasonic generator and a barium titanate oscillator operating at 200 kHz (200 W). The temperature of the solution was kept at approximately 20 °C by a cooling water bath during the sonication. The cylindrical glass vessel (150 mL) had a side arm with a septum for gas bubbling or for withdrawing liquids sample and its bottom was made as thin as possible (1 mm) for good transmission of the ultrasonic waves. The vessel was fixed at 3.8 mm from the oscillator and closed during the sonication. Monoethyl and diethyl 1,2-benzenedicarboxylates were analyzed using a high-performance liquid chromatograph equipped with an ODS-18 column, and the mixture of methanol and phosphate buffer solution was used as the eluent at the flow rate of 1.0 mL min^{-1}.

Table 1. Comparison of the formation rates for monoethyl 1,2-benzenedicarboxylate in alkaline solutions[a]

pH	Formation rate /μM min^{-1}		Enhancement[c]
	Sonication[b]	Non-sonication (Stirring)	
11.0	1.4	0.4	3.5
11.5	3.0	0.7	4.3
12.0	5.4	1.4	3.9
12.5	10.3	2.9	3.6
12.0[d]	4.3	3.9	1.1

[a]Monoethyl 1,2-benzenedicarboxylate was determined as hydrolysis product of 100 μM diethyl 1,2-benzenedicarboxylate. [b]Sonication was performed under an argon atmosphere. [c]Enhancement = sonication / non-sonication. [d]Hydrolysis of 100 μM dimethyl 1,2-benzenedicarboxylate.

Table 1 shows the ultrasonic enhancement on the hydrolysis of aqueous diethyl 1,2-benzenedicarboxylate solutions under alkaline conditions. The formation rates of the monoethyl 1,2-benzenedicarboxylate during non-sonication (stirring) as well as during sonication were dependent on the increased pH. The average ultrasonic enhancement on the hydrolysis was observed to be approximately 3.8 times. This is a fairly significant hydrolysis enhancement compared to the reported previous studies.[2–4] The evolution of gases by the thermal reaction during the hydrolysis by sonication was confirmed. On the other hand, in the sonolytic hydrolysis of dimethyl 1,2-benzenedicarboxylate, its enhancement was not great. In the presence of ultrasounds, it was observed that the dimethyl 1,2-benzenedicarboxylate was not more rapidly hydrolyzed, due to its physicochemical properties, than diethyl 1,2-benzenedicarboxylate under the same conditions.[7] The hydrophobic solute would be expected to concentrate around the cavitation micro-bubbles (i.e., the gas–liquid interfacial region between the cavitation micro-bubble and the bulk solution) during the sonication, due to the partition into the interfacial region although it would not enter the cavitation micro-bubbles. Therefore, the solute with higher hydrophobicity should be likely to be affected by the chemical effect arising from the collapsing cavitation micro-bubbles in the vicinity of the cavitation micro-bubbles.

Figure 1 shows Arrhenius plots of the hydrolysis rate constants of diethyl 1,2-benzenedicarboxylate by non-sonication at pH 12. From the kinetic data, the activation energy (E_a) was experimentally determined to be 49.9 kJ mol^{-1} and the activation parameters, such as $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ were also calculated to be 47.2 kJ mol^{-1}, 98.4 kJ mol^{-1}, and -156.5 $\text{J} \cdot \text{K}^{-1}\text{mol}^{-1}$, respectively. If it is postulated that the sonolytic hydrolysis is a reaction with the activation energy obtained from the non-sonication experiments and the linear Arrhenius-type behavior, the reaction temperature for the sonolytic hydrolysis can be calculated from the Arrhenius plot of the rate constants of the non-sonication hydrolysis (see Figure 1).

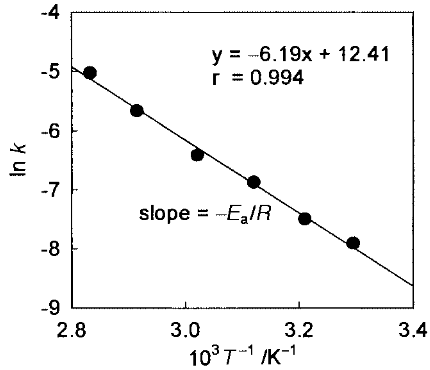

Figure 1. Arrhenius plots of hydrolysis rate constants of diethyl 1,2-benzenedicarboxylate in aqueous solution at pH 12.

Table 2. The average temperatures of solution calculated from Arrhenius plots of the hydrolysis rate constants of diethyl 1,2-benzenedicarboxylate

Dissolved gas[a]	Thermal conductivity /10^{-3}Wm^{-1}K^{-1}	Solubility in water /cmKg^{-1}	k[b] /10^{-3}s^{-1}	Temp. /K
He	151.0	0.86	1.0	320
Ne	49.3	10.5	1.5	327
Ar	17.9	33.6	2.6	337
Kr	9.4	59.4	3.7	344
Xe	5.6	108.0	4.5	348

[a]Dissolved gas was bubbled through the solution for 30 minutes before the sonication. [b]Experimental condition: pH = 12, Temperature = 293 ± 1 K.

Table 2 shows the selected physical properties of the dissolved gas and the results obtained from the sonication under their atmospheres. Under the same conditions, the reaction rate constants for diethyl 1,2-benzenedicarboxylate and the average temperatures of the solution calculated from the experimental equation of Figure 1 were in the order Xe > Kr > Ar > Ne > He. This order was found to be dependent on the nature of the dissolved gas, such as its thermal conductivity and solubility in water. A high water solubility of the dissolved gas may leads to the production of a number of cavitation nuclei. A low conductivity of the dissolved gas is desirable for high collapsing temperature because the heat induced by bubble collapse inside cavitation micro-bubble is rapidly dissipated to the bulk solution. The effects of the dissolved gas on sonolysis have been investigated.[8] The dependence of the dissolved gas on these studies is essentially the same as observed for this study.

The average temperatures of the solution when diethyl 1,2-benzenedicarboxylate was hydrolyzed by the sonication under various dissolved gases were estimated to be higher by 27 to 55 °C than that of the bulk solution. Therefore, the effective heat evolved from the collapse of the cavitation micro-bubbles would result in an enhancement of the hydrolysis in a specific reaction area. And, the micro-mixing effect induced from the violent collapse of the cavitation bubbles should have an effect on the hydrolysis of 1,2-benzenedicarboxylate.

In sonochemistry, three kinds of reaction sites have been proposed, e.g., the inside of the cavitation micro-bubbles where hydroxyl radicals and hydrogen atoms result from the pyrolysis of water vapor under high temperature and pressure conditions, the vicinity of the cavitation micro-bubbles where the high concentration of hydroxyl radicals and a temperature high enough for the thermal degradation of the solute are present, and the bulk solution at ambient temperature and pressure.[1a]

In conclusion, the presented results suggest that the sonochemical effects via heat evolved from the inside of the cavitation micro-bubbles play an important role in the hydrolysis of esters particularly as a hydrophobic solute in the broad area spread over the bulk solution from the gas–liquid interfacial region while the thermal reaction does not take place due to the lower temperature. The application of ultrasound on the ester hydrolysis, which is often conducted under dramatic procedures, may have an important environmental connotation since sonolytic hydrolysis can be carried out under much milder conditions.

References and Notes

1 a) T. J. Mason and J. P. Lorimer, “Sonochemistry: theory, application and uses of ultrasound in chemistry,” Ellis Horwood, West Sussex (1988). b) A. A. Atchely and L. A. Crum, in “Ultrasound: its chemical, physical, and biological effects,” ed. by K. S. Suslick, VHC Pub. Inc., Weinheim (1988), p 1. c) E. B. Flint and K. S. Suslick, *Science*, **253**, 1397 (1991). d) W. B. McNamara, III, Y. T. Didenko, and K. S. Suslick, *Nature*, **401**, 772 (1999). e) Y. T. Didenko, W. B. McNamara, III, and K. S. Suslick, *J. Phys. Chem. A*, **103**, 10783 (1999).

2 a) J. N. Chen and W. M. Kalback, *Ind. Eng. Chem., Fundam.*, **6**, 175 (1967). b) S. Fogler and D. Barnes, *Ind. Eng. Chem., Fundam.*, **7**, 222 (1968).

3 S. Moon, L. Duchin, and J. V. Cooney, *Tetrahedron Lett.*, **20**, 3917 (1979).

4 D. S. Kristol, H. Klotz, and R. C. Parker, *Tetrahedron Lett.*, **22**, 907 (1981).

5 I. Hua, R. H. Höchemer, and M. R. Hoffmann, *J. Phys. Chem.*, **99**, 2335 (1995).

6 a) T. Ando, M. Fujita, T. Kimura, and Y. Kondo, *J. Org. Chem.*, **63**, 6048 (1998). b) A. Tauber, H. -P. Schuchmann, and C. von Sonntag, *Chem. Eur. J.*, **5**, 2198 (1999).

7 The physicochemical properties of dimethyl and diethyl 1,2-benzenedicarboxylate are as follows; solubility in water (g L^{-1}) = 4.2, 1.1; octanol–water distribution constant (log K_{ow}) = 1.61, 2.38; vapor pressure (mmHg, 25 °C) = 0.002, 0.001, respectively.

8 a) F. R. Young, *J. Acoust. Soc. Am.*, **60**, 100 (1976). b) T. Kondo, J. Gamson, J. B. Mitchell, and P. Riesz, *Int. J. Radiat. Biol.*, **54**, 955 (1988). c) P. Riesz and T. Kondo, *Free Rad. Bio. Med.*, **13**, 247 (1992). d) I. Hua and M. R. Hoffmann, *Environ. Sci. Technol.*, **31**, 2237 (1997). e) Y. Nagata, H. Okuno, Y. Mizukoshi, and Y. Maeda, *Chem. Lett.*, **2001**, 142.