

Sonochemistry of Selected Hydrocarbons, Sulfur-containing  
and Nitrogen-containing Organic Compounds in Aqueous  
Solutions and Nonaqueous Liquids

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# 1 Introduction

The European Society of Sonochemistry defined sonochemistry as the application of ultrasound to chemical reactions and processes [1]. Hence, Sonochemistry is chemistry assisted/enhanced by ultrasound.

Ultrasound can enhance or promote chemical reactions and mass transfer and offer the potential for shorter reaction cycles, cheaper reagents, and less extreme physical conditions. So far, ultrasound has been applied in studies of cleaning, organic synthesis, catalysis, extraction, emulsification, material processing, food processing, and wastewater treatment [2, 3].

Richards and Loomis [4] noticed the first chemical effects of high frequency sound waves in 1927. The acceleration effects of ultrasound on the reduction of  $K_2MnO_4$  by oxalic acid, hydrolysis of dimethyl sulfate, and reduction of  $KIO_3$  by sulfurous acid were reported. In 1929, Schmitt et al. [5] reported the oxidation promoted by ultrasonic radiation. The formation of  $H_2O_2$  and the cleavage of C-Cl bonds of  $CCl_4$  induced by ultrasound in aqueous solutions were first found. Soon after the advent of inexpensive and reliable laboratory generators of high-intensity ultrasound, a renaissance of sonochemistry occurred in the 1980's, focusing on the application of ultrasound in the treatment of wastewater containing organic pollutants [6].

Currently the thermal theory is widely used to explain the origins of homogeneous sonochemistry [7, 8]. "Intense ultrasonic waves traveling through liquids generate small cavities that enlarge and implode, creating tremendous heat. These extreme conditions provide an unusual chemical environment [9]". These imploding cavities (or collapsing bubbles) are called "hot spots". Such a hot spot is the source of homogeneous sonochemistry; it has a temperature of roughly 5000 K, a pressure of about 1000 atmospheres, a diameter of 100 microns, a lifetime considerably less than a microsecond, and heating and cooling rates above 10 billion K per second [10].

The collapsing bubbles have both physical and chemical effects. The physical effects can enhance the reactivity of a catalyst by enlarging the surface area, or accelerate a reaction by proper mixing of reagents. Chemical effects of ultrasound enhance reaction rates due to the formation of highly reactive radical species formed in the collapsing cavities. In some cases, ultrasonic irradiation can increase reactivity by nearly one million-fold. The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis [11].

These bubbles filled with vapors and gases produce radicals during such an implosion. These implosions are the spectacular part of sonochemistry. Each one of these imploding bubbles can therefore be seen as a micro reactor. The high temperatures and pressures created during the cavitation collapse can even produce a flash of light (sonoluminescence) [9, 12-15].

In the unusual chemical environment, water undergoes thermal decomposition to release atomic and radical species ( $\cdot\text{H}$ ,  $\cdot\text{OH}$ ) [16-18]. These species can recombine to form hydrogen and hydrogen peroxide, or attack organic substrates. Mostly, volatile organic compounds in the imploding cavities or nearby participate in the primary sonochemical reaction and are pyrolyzed during sonication [19-22].

Sonochemistry is strongly affected by the acoustic frequency, acoustic intensity, bulk liquid temperature, dissolved gas and solvent. Generally, the rate of homogeneous sonochemical reaction decreases with a rise of the bulk liquid temperature [9, 23, 24]. The rate of  $\text{H}_2\text{O}_2$  formation and the sonolysis of organic compound are strongly dependent on the dissolved gas, because the temperature inside the collapsing bubble is related to the vapor pressure of the solvent, the ratio of specific heats and the thermal conductivity of the gas [9, 25-28]. In general, the maximum temperature reached inside a collapsing transient bubble is proportional to the ratio of specific heats of dissolved gas, and inversely proportional to vapor pressure of solvent [23, 24].

Both the acoustic frequency and intensity affect the cavitation bubble size, the maximum collapse time, and the temperature. The cavitation bubble diameter is much larger at 20 kHz than at 500 kHz. The maximum collapse time for a cavitation bubble is, therefore, much shorter at 500 kHz than at 20 kHz [29]. In general, an increase in power density results in an increase in the sonochemical reaction rate. However, it is often observed experimentally that rates eventually begin to diminish again as one continuously increase the acoustic amplitude [19, 30].

The earlier investigation of sonolyses of organic compounds in aqueous solutions (aquasonolysis) have focused, inter alia, on aromatic compounds, chlorinated aliphatic and aromatic hydrocarbons and phenols [6-8]. So far, only little is known about sonolyses of organic sulfur-containing [20, 26, 31] and nitrogen-containing compounds [21, 32]. Furthermore, the influences of the natures of substrates themselves on sonolyses have rarely been stated. Therefore, the mechanisms of sonolyses of organic compounds in aqueous solutions are not clearly interpreted [19, 33-36].

In 1980s, Suslick et al. [37-40] reported the first sonochemistry of discrete organometallic complexes and demonstrated the effects of ultrasound on metal carbonyls. Sonolyses of pure alkane and other hydrocarbons have also been reported [41-43]. However, the sonochemistry of solutes in organic liquids and pure organic liquid also remains largely unexplored.



The study aims at gaining further understanding of the sonochemical mechanisms and kinetics of volatile organic compounds in aqueous and nonaqueous solutions. After a detail introduction to sonochemistry (Chapter 2) and the description of equipments of experiments and analyses (Chapter 3), Chapter 4 is dedicated to the sonolytic kinetics and products of the selected  $C_6H_X$  hydrocarbons, thioethers, thiophenes, and N-heterocyclic compounds in aqueous solutions. Additionally, the sonolytic rates, the rates of DPPH trapping, and products of the above-mentioned compounds in pure organic liquids or organic solvents are reported in Chapter 5.

The effects and the roles of volatility, hydrophobicity, thermostability, initial concentration of the substrates, liquid temperature, and ultrasonic power on sonolyses of model compounds in aqueous solutions and in nonaqueous liquids are discussed in Chapter 6. Sonochemical mechanisms of the model compounds are also proposed in this chapter. Finally, Chapter 7 summarizes the conclusions drawn from this extensive study.

## 2 Theoretical Part

### 2.1 Ultrasound

Sound is our experience of the propagation of pressure waves through some physical elastic medium, such as air, or liquid. The pressure waves are generated from some type of mechanical disturbance. Generally, human hearing can not go beyond about 18 kHz, sound beyond this limit is inaudible and is defined as ultrasound [7]. Ultrasound as sound above 20 kHz and up to 100 kHz can generate greater acoustic energy, and affect chemical reactivity [3]. Up to now, the ultrasound range applied in sonochemistry has been extended to 2 MHz. Figure 2-1 shows the frequency ranges of sound and the applied frequencies in the field of sonochemistry.

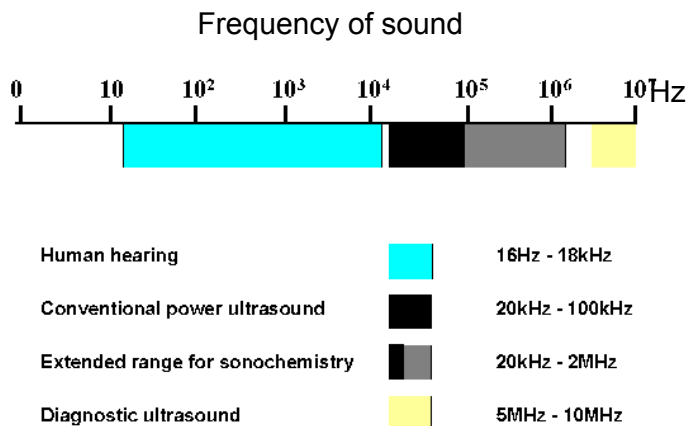


Figure 2-1 Frequency ranges of sound and its application

Source: T. J. Mason [44]

### 2.2 Acoustic Cavitation

Acoustical energy is mechanical energy, and it is not absorbed by molecules. Liquids irradiated with ultrasound can produce bubbles, when the pressure within the liquid drops sufficiently, and

lower than the vapor pressure of the liquid. This process is called “cavitation”. Turbulent flow, laser heating, electrical discharge, boiling, and radiolysis can also cause bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. Figure 2-2 shows three discrete stages of acoustic cavitation: nucleation, bubble growth, and collapse in a liquid. In principle, sonochemistry derives from acoustic cavitation [11].

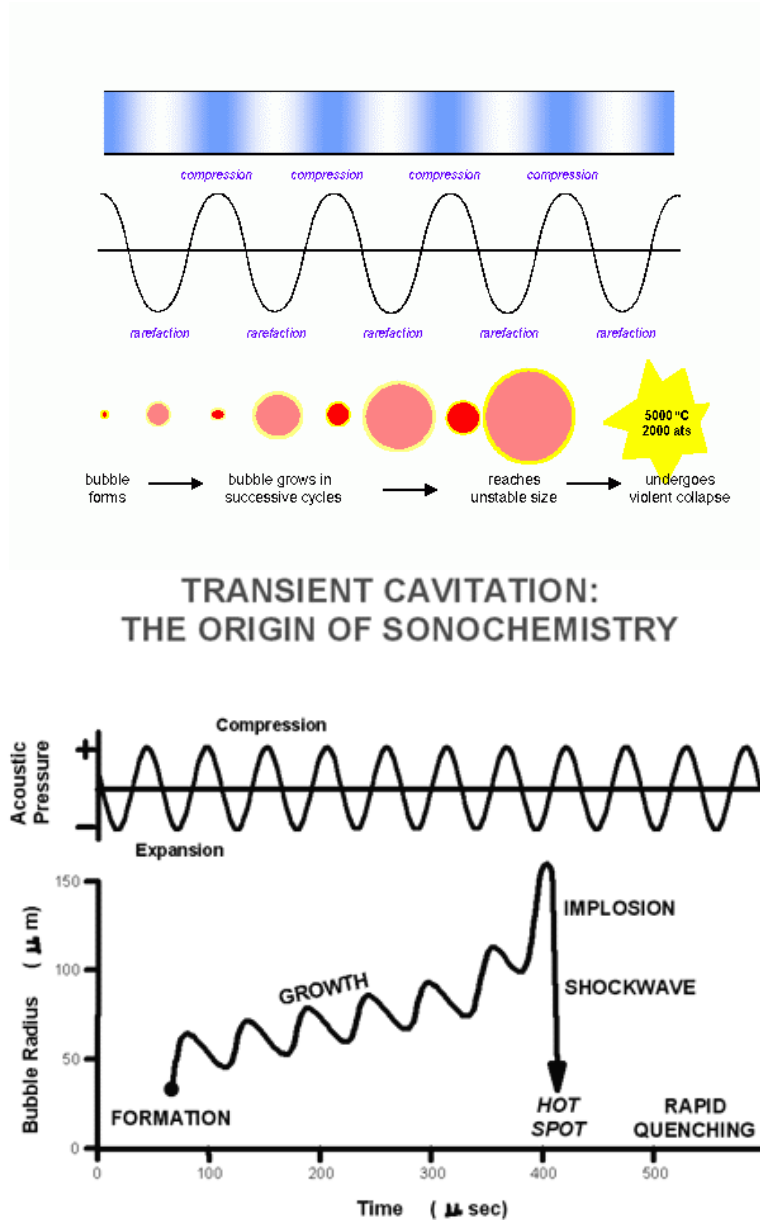


Figure 2-2 Generation and life of an acoustic bubble

Source: T. J. Mason [45]; K. S. Suslick [46].

Two forms of cavitation are known [7]: stable and transient. Stable cavitation means that a bubble oscillates many times with limited change about its equilibrium radius. While transient cavitation, a short-lived bubble undergoes large excursions of size in a few acoustic cycles and may terminate in a violent collapse. Both stable and transient cavitation may occur simultaneously in a solution and a bubble undergoing stable cavitation may change to transient cavitation.

The sizes of the cavities before collapse were calculated to be about 170  $\mu\text{m}$  at 20 kHz, 4.6  $\mu\text{m}$  at 500 kHz, and about 3.3  $\mu\text{m}$  at 1 MHz. The bubbles are short lived, with maximum lifetimes near 0.4  $\mu\text{s}$  and 10  $\mu\text{s}$  at 500 and 20 kHz respectively [7, 8, 11, 29].

## 2.3 Mechanisms and Sites of Sonochemical Reactions

### 2.3.1 Mechanisms of Sonochemical Reactions

There are three different theories about cavitation - the hot spot, the electrical discharge, and the plasma theory. Currently, the hot spot theory is the most popular one. The collapse of cavity generates extreme energy for chemical and mechanical effects. It has been experimentally estimated that drastic conditions exist inside the medium for an extremely short time: temperatures of 5000 K and pressures of 500 ~ 1000 atm inside the collapsing cavity [11, 47]. This ‘adiabatic’ heating in the bubble interior is even thought to reach around 10000 ~ 20000 K [48]. Additionally, the evidence for nuclear emission during acoustic cavitation in deuterated acetone was observed in 2002 [49]. It means that the hot bubble implosion conditions achieve  $10^6$  to  $10^7$  K, as required for nuclear fusion reactions.

The size, lifetime and fate of a cavitation bubble depend on the following parameters: acoustic frequency and intensity, physicochemical properties of solvent and dissolved gas, and external parameters (temperature, pressure). However, it should be noted that there is often no simple relationship. Assuming adiabatic bubble collapse, Noltingk [23] and Neppiras [24] calculated the maximum temperature and pressure reached inside a collapsing transient bubble by:

$$T_{\max} = \frac{T_0 P_a (\gamma - 1)}{P_v} \quad (E 2-1)$$

$$P_{\max} = P_v \left\{ \frac{P_a (\gamma - 1)}{P_v} \right\}^{[\gamma / \gamma - 1]} \quad (E 2-2)$$

where  $T_0$  is the liquid temperature,  $P_a$  is the acoustic pressure at initiation of collapse,  $\gamma$  is the ratio of specific heats of dissolved gas or vapor, indicating how much heat is released from the gas

during the adiabatic compression.  $P_v$  is the vapor pressure of solvent. Thus, the vapor pressure of solvent, type of dissolved gas, and aqueous temperature are the most important factors for the bubble collapse.

A remarkable event during the cavitation collapse is the emission of light under certain conditions (sonoluminescence). Sonoluminescence is definitively due to chemiluminescence from species produced thermally during cavitation collapse and is not attributable to electric microdischarge [9]. The thermal theory of sonochemistry holds that the sonoluminescence arise from hot molecules and radicals formed in the cavitation hot spot by molecules cleavage or rearrangement, followed by atomic and radical recombination, and thermal and chemical quenching.

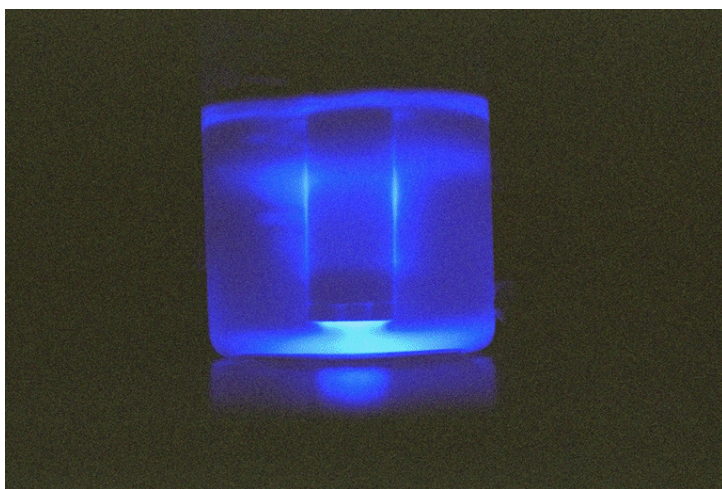


Figure 2-3 Sonoluminescence from a high intensity ultrasonic horn

Source: K. S. Suslick [50]

Sonoluminescence (SL) was first discovered in 1934 by Frenzel and Schultes [51]. These researchers saw multiple-bubble sonoluminescence (MBSL), i.e. the glow from many bubbles of air in water (Figure 2-3). Since the glow for bubbles is so faint, it must be viewed in a darkened room. Single-bubble sonoluminescence (SBSL), however, can be seen in a lighted room. Sonoluminescence spectra from solutes and solvents were often applied to measure the temperature of cavitation [25, 52, 53].

Furthermore, the cavitation collapse causes a couple of strong physical effects outside the bubble: shear forces, jets and shock waves [11]. Near an extended solid surface, cavitation collapse is nonspherical and drives high-speed jets of liquid to the surface. This process can produce newly exposed, highly heated surfaces. Shock waves from cavitation in liquid-solid slurries produce high-velocity interparticle collisions, the impact of which is sufficient to melt most metals. Thus, there are basically two groups of effects: radical and mechanical effects, such as [7, 8]:

- Sonolyses of molecules: homolytic fragmentation to radicals, rupture of polymers, generation of excited states, cell disruption;
- Effects in liquid-liquid systems: improved mass transfer, emulsification, increase of the effect of phase transfer catalysts or even their replacement;
- Effects in gas-liquid systems: degassing of liquids or melts, atomization of liquids in air, thin film preparation;
- Effects in liquid-solid: heterogeneous sonochemistry.

### 2.3.2 Sites of Sonochemical Reactions

As the bubble expands, gases dissolved in the liquid, volatile solutes and solvent enter the bubble. At the point of adiabatic collapse, some of these substances are trapped inside the hot bubble and start to react [48]. Three possible reaction sites of a collapsing bubble in a homogeneous liquid are illustrated in Figure 2-4: the cavity interior, the bubble vicinity and the bulk solution.

Suslick et al. [41, 47, 54] used the sonochemistry of n-alkanes and volatile metal carbonyls to determine the sonochemical reactions site. They discovered that the linear dependence of the observed rate coefficients or rates on vapor pressures of n-alkanes or metal carbonyl, and suggested that the reaction occurs in the gas phase. The effective temperatures of these hot spots were measured at  $\sim 5200$  K in the gas-phase reaction zone and  $\sim 1900$  K in the initially liquid zone. In addition, using a simple thermal conduction model, the liquid reaction zone was estimated to be about 200 nm thick and to have a lifetime of less than 2  $\mu$ s [47].

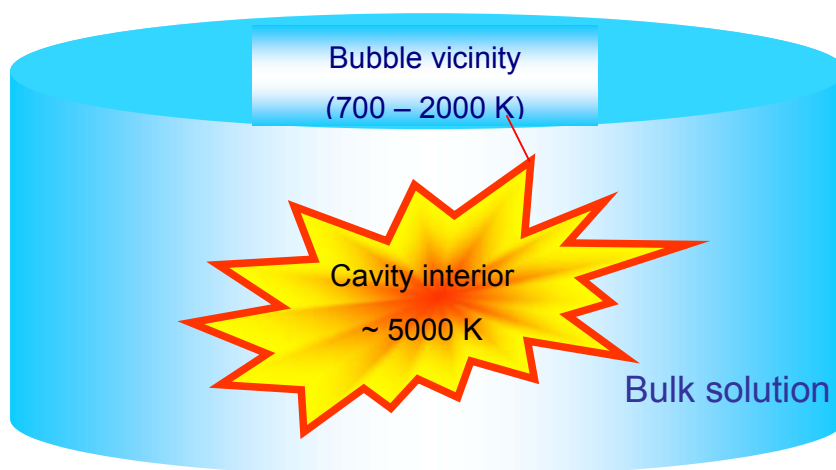


Figure 2-4 Acoustic cavitation and reaction sites in a homogeneous liquid

Source: T. J. Mason [45]

## 2.4 Kinetics of Sonochemical Reactions

More attention has been paid to the investigations of the sonochemical kinetics of organic compounds in aqueous solutions. The sonolytic rate is defined as the rate of the disappearance of a substrate, and calculated by the change in concentration for a given period of time. The sonolytic rate is proportional to the concentration of substrate. The proportionality constant ( $k_{obs}$ ) is called sonolytic rate constant. In general, pseudo-first-order kinetics is commonly employed in mechanistic studies of the sonochemistry in aqueous solution. The rate law is [55]:

$$v = -\frac{d[C]}{dt} = k_{obs} \times [C] \quad (E\ 2-3)$$

where  $v$  is the sonolytic rate,  $d[C]$  is the change in concentration of substrate,  $dt$  is the given period of time,  $[C]$  is the concentration of substrate, and  $k_{obs}$  is the pseudo-first-order rate constant.

Equation (E2-3) is rearranged and integrated using standard algebraic methods. The results are shown in equation (E2-4), where  $[C]_0$  is the initial substrate concentration, and  $[C]_t$  is its concentration at the time  $t$ :

$$\ln \frac{[C]_t}{[C]_0} = -k_{obs} \times t, \text{ or } \frac{[C]_t}{[C]_0} = e^{-k_{obs} \times t} \quad (E\ 2-4)$$

The integrated rate equations for pseudo-first-order kinetics are often employed for the investigation of sonolytic rates in aqueous solutions.

The Arrhenius equation expresses the dependence of the rate constant on the reaction temperature [55]:

$$\ln k = \ln A - \frac{E_a}{RT}, \text{ or } k = A \times e^{-E_a / RT} \quad (E\ 2-5)$$

where  $A$  is the preexponential factor,  $E_a$  is the Arrhenius activation energy,  $T$  is the absolute reaction temperature,  $R$  is the gas constant, and  $k$  is the rate constant. It indicates that the reaction rate increases with an increase in reaction temperature. In combination with the activation parameter ( $A$  and  $E_a$ ) from thermochemistry data, the Arrhenius equation is often used to evaluate the temperature of reaction sites [35, 41, 47, 56].

The disappearance rate of a radical scavenger in organic media is often used to evaluate the sonolytic rate of the organic liquid, and the formation rates of products are directly used to analyze the selectivity of sonochemical reactions of organic liquids [41, 43].

## 2.5 Sonochemistry of Organic Compounds in Aqueous Solutions

The formation of  $\text{H}_2\text{O}_2$  during the sonolysis of water and the ultrasonic cleavage of organic compounds in water were first reported by Schmitt et al. in 1929 [5]. The sonolysis of water produces  $\text{H}_2\text{O}_2$ , and the C-Cl bond of  $\text{CCl}_4$  in KI-starch solution is cracked during the ultrasonic irradiation. In 1950's, the aqueous sonochemistry was revived. Weissler et al. [19] discovered that aqueous solutions of  $\text{CCl}_4$  liberated  $\text{Cl}_2$  upon ultrasonic irradiation in the absence of  $\text{O}_2$ , and greatly accelerated the formation of  $\text{I}_3^-$  in aqueous iodide solutions. The role of free radicals in the formation of  $\text{H}_2\text{O}_2$  by ultrasonic waves was indicated in 1959 [16]. Zechmeister and his co-workers [20-22] first reported the ultrasonic cleavage of the benzene ring and heterocycles. Since 1970, more attention has been paid to the secondary reactions of OH and H radicals. Spurlock and his co-workers [26, 33] reported that the irradiation of aqueous suspensions of thioethers gives mostly sulfoxides and sulfonic acids, and aldehydes give mostly carboxylic acids. Up to 1980, along with the development of environmental sonochemistry, aqueous sonochemistry reached a climax. The sonochemistry of a large number of organic compounds of environmental interest in aqueous solutions has been studied.

In 2001 Adewuyi [6] published an introductory and specialized review about applications of sonochemistry in environmental science and engineering. Environmental sonochemistry is a rapidly growing area that deals with the destruction of organics in aqueous solutions. Table 2-1 shows a summary of aqueous sonochemistry of organic compounds.

Moreover, sonochemistry in aqueous solution is strongly affected by a variety of parameters, including acoustic frequency, acoustic intensity, bulk temperature and applied pressure, and dissolved gas [7]. In addition, the physicochemical properties and initial concentration of organic solutes can also influence the aquasonolysis.

### 2.5.1 Mechanisms and Reaction Sites of Aquasonolysis

The organic sonochemical reactions in aqueous solutions are divided into two groups [8]:

- (1) Reactions at very high temperature and pressure during the collapse of cavitation bubbles.
- (2) Radical reactions taking place at the gas-liquid interface of the bubbles and bulk liquid.



Table 2-1 Aqueous sonochemistry of organic compounds

	Substrate	Intermediates and products	Authors*	Ref.
Aliphatic hydrocarbons	methane	H <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>3</sub> -C <sub>4</sub> hydrocarbons, CO, CO <sub>2</sub> , CH <sub>2</sub> O	Henglein, 1985	[57]
	methane	H <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , CO, C <sub>3</sub> H <sub>8</sub> , C <sub>3</sub> H <sub>6</sub>	Hart, 1990	[58]
	acetylene	H <sub>2</sub> , CO, CH <sub>4</sub> , HCOOH, CH <sub>3</sub> COOH, HCHO, CH <sub>3</sub> CHO, other C <sub>2</sub> -C <sub>8</sub> hydrocarbons, insoluble soot, C <sub>6</sub> H <sub>6</sub> , styrene, naphthalene, and phenylacetylene	Hart, 1990	[59]
Aromatic hydrocarbons	benzene	C <sub>2</sub> H <sub>2</sub> , CO	Lamy, 1993	[60]
	toluene	HCHO, phenolic hydroxyls, benzoic acid	Soudagar, 1995,2	[61]
	toluene	benzaldehyde, bibenzyl	Bian, 2001	[62]
Halogenated aliphatic hydrocarbons	ethylbenzene	benzene, toluene, styrene, cumene propylbenzene, diphenylmethane, 1,2-diphenylethane, benzaldehyde, acetophenone, phenylacetylene.	De Visscher, 1997	[63]
	tetrachloromethane	Cl <sub>2</sub> , CO <sub>2</sub> , HCl, C <sub>2</sub> Cl <sub>6</sub> , C <sub>2</sub> Cl <sub>4</sub> , HOCl	Schmitt, 1929; Weissler, 1950; Liu, 1934; Griffing, 1950; Jennings, 1961; Chendke, 1983; Alippi, 1992; Hua, 1996, Hung, 1998; Hung, 1999; Rajan, 1998	[5, 19, 64-71] [72]]
	dichloromethane	Cl <sup>-</sup> , Cl <sub>2</sub>	Prakash, 1958	[73]
	ethyl iodide	I <sub>2</sub> +I <sup>-</sup>	Prakash 1965	[74]
Halogenated aromatic compounds	trichloromethane	Cl <sup>-</sup> , H <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub>	Inazu, 1993	[75]
	trichloroethylene	Cl <sup>-</sup> , H <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> HCl, C <sub>2</sub> Cl <sub>2</sub> , C <sub>4</sub> Cl <sub>2</sub> , C <sub>2</sub> Cl <sub>4</sub> , C <sub>4</sub> HCl <sub>3</sub> , C <sub>4</sub> Cl <sub>4</sub> , C <sub>4</sub> HCl <sub>5</sub> , C <sub>4</sub> Cl <sub>6</sub>	Drijvers, 1996; Drijvers, 1999; Dewulf, 2001; Kang, 2001	[76-79]
	bromobenzene	Br <sup>-</sup> , C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>2</sub>	Zechmeister, 1955	[20]
Alcohols	o-dichlorobenzene	Cl <sup>-</sup>	Prakash 1965	[74]
	chlorobenzene	Cl <sup>-</sup> , CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>4</sub> , C <sub>4</sub> H <sub>2</sub> , phenylacetylene, benzene, chlorophenols, non-chlorinated mono- and dicyclic hydrocarbons	Lamy, 1993; Kruus, 1997; Drijvers, 1998; Petrier, 1998.	[60, 80] [81] [82]
	iodobenzene	I <sup>-</sup> , C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>2</sub>	Zechmeister, 1955; Prakash 1965	[20, 74]
	polychlorinated biphenyls	biphenyl, ethyl benzene, diethylbiphenyl, dibutylbiphenyl, phenol, propylphenol, di-t-butyl phenol, chloride	Zhang, 2000	[83]
Phenols	cyclohexanol	C <sub>2</sub> H <sub>2</sub>	Currell, 1968	[84]
	methanol	H <sub>2</sub> , CH <sub>2</sub> O, CO, CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> under Ar. CO <sub>2</sub> , CO, HCOOH, CH <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> under O <sub>2</sub>	Buettner, 1991	[85]
	alcohol	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>2</sub>	Koike, 1992	[86]
	t-butanol	CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>4</sub> H <sub>6</sub>	Tauber, 1999	[87]
Organic sulfur compounds	phenol	hydroquinone, catechol, CO <sub>2</sub> , benzoquinone	Chen, 1971; Okouchi, 1992; Lamy, 1993; Petrier, 1994; Berlan, 1994; Takizawa, 1996.	[60, 88-92]
	chlorophenol	chlorohydroquinone, chlorocatechol, hydroquinone, catechol, chloride at pH 11, glyoxylic acid at pH 3, CO <sub>2</sub>	Lamy, 1993; Berlan, 1994; Serpone, 1994; Ku, 1997.	[60, 92-94]
Organic nitrogen compounds	iodothiophene in silver nitrate solution	AgI, Ag <sub>2</sub> S, silver acetylide, and silver diacetylide	Zechmeister, 1955;	[20]
	dibutyl sulfide	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO, n-butylsulfonic acid, butyric acid, CO, C <sub>2</sub> H <sub>4</sub> , CH <sub>4</sub>	Spurlock, 1970	[26]
	carbon disulfide	sulfate under air, amorphous carbon and monoclinic sulfur,	Entezari, 1997; Appaw, 2002; Adewuyi, 2002	[95-97]
	benzothiophene	hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophenedione	Kim, 2002	[31]
Organic nitrogen compounds	pyridine	HCN, C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>2</sub>	Zechmeister, 1956	[21]
	pyridine	HCN, C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>2</sub>	Currell, 1963	[32]
	ethylenediamine	NH <sub>3</sub>	Anbar, 1964	[98]
	RCH <sub>2</sub> NH <sub>3</sub>	H <sub>2</sub> , CH <sub>4</sub> , NH <sub>3</sub> , RCHO, RCH <sub>2</sub> OH	Fayter, 1974	[99]
	4-nitrophenol	4-nitrocatechol, CO <sub>2</sub> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , p-benzoquinone, hydroquinone	Kotronarou, 1991; Barbier, 1996; Cost, 1993; Hua, 1995; Tauber, 2000	[35, 100-103]
	3-chloroaniline	Cl <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CO, CO <sub>2</sub>	David, 1998	[104]
nitrobenzene	nitrophenol, 4-nitrocatechol	Hung, 2000	[105]	

\* Only first author is listed.

### 2.5.1.1 Sonolysis of Water

Cavitation bubbles implosion and fragmentation produce microregions of extreme conditions. Because of the very high temperature and pressure, water undergoes thermal decomposition to release radical species ( $\cdot\text{H}$ ,  $\cdot\text{OH}$ ) as shown below [18, 29]:



The radicals recombine to form hydrogen and hydrogen peroxide:



Hart and Henglein [17] noted that  $\text{HO}_2\cdot$  radicals could be formed in the presence of oxygen.  $\text{HO}_2\cdot$  radicals can also produce  $\text{H}_2\text{O}_2$ :



In general,  $\text{H}_2\text{O}_2$  is formed by three parallel pathways: from the water, from oxygen atoms, and from oxygen molecules [98].  $\text{H}_2\text{O}_2$  formation follows zero-order kinetics [100]. The concentration of hydroxyl radicals at the bubble interface has been estimated to be  $4 \text{ mmol L}^{-1}$  [106]. The apparent  $\text{H}_2\text{O}_2$  production rates at 205 kHz with  $244 \text{ W L}^{-1}$  power density under either Ar or  $\text{O}_2$  were found to be identical, i.e.,  $3.5 \times 10^{-4} \text{ mmol L}^{-1} \text{ min}^{-1}$  [107]. Kotronarou et al. [35, 108] determined the sonolytic production rates of  $\text{H}_2\text{O}_2$  in air-saturated water is  $2.40 - 2.52 \times 10^{-3} \text{ mmol L}^{-1} \text{ min}^{-1}$  at 24 kHz and  $3360 \text{ W L}^{-1}$ .

### 2.5.1.2 Sonolyses of Organic Compounds

Weissler et al. [19] demonstrated that free chlorine is not liberated from  $\text{CCl}_4$  by activated oxygen or a similar oxidant during the ultrasonic irradiation of KI solution with a large excess of  $\text{CCl}_4$ , but  $\text{CCl}_4$  itself participates in the primary sonochemical reaction. The C-Cl bonds are broken by the large mechanical or electrical forces generated during the collapse of cavitation bubbles. In fact, in addition to the direct high temperature decomposition of water, direct pyrolyses of volatile organic solutes such as carbon tetrachloride also occurs in the vapor-phase of the bubble or at the hot interfacial region [29]:



In general, pyrolysis of volatile organic compounds (VOCs) in collapsing bubbles is the predominant degradation pathway. By analyses of products from sonochemical degradation of trichloroethylene and ethylbenzene in aqueous solutions, the pyrolysis is an important pathway [63, 76]. The sonochemical degradation of either chlorobenzene or methyl tertiary butyl ether (MTBE) is not suppressed by radical scavenger (n-butanol), and the same products were observed during sonolyses and pyrolyses [80, 109]. Furthermore, Tauber et al. [87] found that  $\cdot\text{OH}$  radical-induced reactions in solutions are insignificant during the sonolysis of t-butanol. Its gas-phase concentration within the bubble enhanced by a certain degree of hydrophobicity causes  $\cdot\text{OH}$  radicals to be intercepted before they can reach the aqueous phase. Kang et al. [79] observed the sonochemical destruction rates of trichloroethylene, tetrachloroethylene, benzene and toluene in the absence or presence of bicarbonate (radicals scavenger). Bicarbonate affects trichloroethylene decomposition insignificantly at the bicarbonate range of 1-10 mmol L<sup>-1</sup>. Therefore, the thermal decomposition is the predominant degradation pathway of the sonochemical destruction of the volatile organic compounds in aqueous solutions.

### 2.5.1.3 $\cdot\text{OH}$ radical Reactions

The sonolysis of water can produce both strong oxidants and reductants that are capable of causing secondary oxidation and reduction reactions [110]. Many ultrasonic oxidation products of organic compounds at the gas-liquid interface of the bubbles or bulk liquid were reported [26, 33, 35, 60, 80, 82, 92-94, 100-103, 111, 112]. Both  $\cdot\text{OH}$  radical and  $\text{H}_2\text{O}_2$  were considered to diffuse into the bulk solution and attack solutes which are not transported to the cavitation bubble [17]. However, the oxidation processes mainly play a role during the sonication of hydrophilic organic compounds, and these oxidation processes are not the major decomposition routes for hydrophobic volatile organic compounds.

Lamy et al. [60] reported the ultrasonic degradation of benzene, chlorobenzene, phenol, and chlorophenol in water. Benzene and chlorobenzene disappeared faster than phenol and chlorophenol. During the decomposition of phenol and chlorophenol at 500 kHz, hydroxylated

compounds were observed. However, acetylene and CO were observed during the decomposition of benzene and chlorobenzene, without hydroxylated by-products.

Sperpone et al. [94] carried out the ultrasonic decomposition of three chlorophenols. They found these phenols totally transformed to dechlorinated, hydroxylated intermediates in about 10 h for 2-chlorophenol and 3-chlorophenol at 20 kHz, and 15 h for 4-chlorophenol. In addition, they demonstrated that the reaction takes place in the bulk solution at low concentrations of chlorophenol, while at higher concentrations, the reaction occurs predominantly at the gas bubble/liquid interface.

Dewulf et al. [78] investigated the ultrasonic degradation of trichloroethylene and chlorobenzene at micromole concentration ranges, where  $\cdot\text{OH}$  radical-induced degradation becomes significant. Simulations showed that at initial concentrations of chlorobenzene  $> 1000 \mu\text{M}$ , degradation due to pyrolysis accounts for over 99.97%, but at concentrations between 1 and 5  $\mu\text{M}$ , the  $\cdot\text{OH}$  radical mechanism contributed 48.5% of the total degradation.

Furthermore, reactions in supercritical water at the interfacial region have been reported [56]. The supercritical phase of water exists above the critical temperature ( $T_c$ , of 647 K) and the critical pressure ( $P_c$ , of 221 bar), and has physical characteristics intermediate like both gas and liquid. Enhanced combustion and hydrolyses of organic compounds have been observed in supercritical water.

### 2.5.2 Effects of Acoustic Frequency

Earlier researchers noted that the sonochemical reaction rate shows an irregular variation with increasing frequency [19]. Generally, sonochemical reaction occurs more quickly at higher frequencies, and there is an optimum frequency range [113]. There are several reasons for enhanced sonochemistry at higher frequencies, including the enhancement of the collapse intensity of individual bubbles. Differences in rectified diffusion and microstreaming at higher frequencies may result in a greater number of cavitation bubbles [18]. However, at a very high frequency, the rarefaction (and compression) cycles are very short. The time required for the rarefaction cycle is too short to permit a cavitation bubble to grow to a size sufficient to cause optimal disruption of the liquid [107].

Furthermore, acoustic frequency affects the size of cavitation bubble and the collapse time. At 20 kHz, the cavitation bubble diameter is estimated to be 170  $\mu\text{m}$  while at 500 kHz it is 4.6  $\mu\text{m}$  [8, 29]. The maximum collapse time for a cavitation bubble is, therefore, much shorter at 500 than at 20 kHz (0.4  $\mu\text{s}$  and 10  $\mu\text{s}$ , respectively). When the life of these bubbles increases, transient species

produced by the decomposition of water have enough time to recombine inside the hot bubble. This recombination restores water, therefore decreasing the efficiency of the process. At 500 kHz, radicals are ejected more rapidly and combine in the cold bubble outer shell forming  $H_2O_2$ .

So far, the effects of frequency were focused on the oxidation rate of iodide, formation rates of  $H_2O_2$  and/or  $\cdot OH$  radical, and decomposition rates of organic solutes in water. The summaries of the effects of frequency on the sonochemistry of aqueous solutions are listed in Table 2-2, Table 2-3, and Table 2-4 respectively. In general, a higher frequency is favorable at the point of view of energy efficiency of the sonochemical processes [30], and the optimum frequency range is between 200 ~ 900 kHz.

Table 2-2 *Effects of frequency on ultrasonic oxidation of iodide*

Range of frequency [kHz]	Other conditions	Oxidation rates of iodide	Authors*	References
400 ~ 1500	at constant power input	An irregular variation in iodine yield with increasing frequency.	Weissler, 1950	[19]
20 ~ 80	-	The rate reaches a maximum at 59 kHz on the oxidation of iodide to iodine.	Cum, 1992	[114]
20, 900	in the presence of air	The rate of oxidation of iodide per unit power at 900 kHz can be more than 30 times greater than that at 20 kHz.	Entezari, 1994	[115]
20, 900	with equal ultrasonic tip area	The real effect of frequency on the oxidation is 1.2 – 2 times greater at 900 than at 20 kHz.	Entezari, 1996	[116]
205, 358, 618, 1078	identical power density	The optimum frequency for $I_2$ production is located between 358 and 618 kHz.	Kang, 1999	[107]

\* Only first author is listed.

Table 2-3 *Effects of frequency on formation rates of  $H_2O_2$  and/or  $\cdot OH$  radicals*

Range of frequency [kHz]	Other conditions	Formation rates of $H_2O_2$ or $\cdot OH$ radical	Authors*	References
280, 610, 800,	pure water, Under $O_2$ and Ar, $9.4 W cm^{-2}$	At 280 kHz: highest $H_2O_2$ formation.	Spurlock, 1970	[26]
20, 500	Ar and air	It is greater at 500 than at 20 kHz.	Petrier, 1992; 1994	[90, 117]
20 ~ 60	-	$\cdot OH$ production increases with the frequency.	Mason, 1994	[118]
20, 500	same ultrasonic power and transducer diameter	It is 3.3 times greater at 500 than at 20 kHz.	Barbier, 1996	[100]
20, 40, 80, 500	Kr, Ar, He, $O_2$	Sonication at 500 and 80 kHz yield faster rates than sonication at 20 and 40 kHz for all saturating gases.	Hua, 1997	[18]
20, 200, 500, 800	-	The formation rates of $\cdot OH$ radicals, $H_2O_2$ have a maximum value at 200 kHz.	Petrier, 1997;	[119, 120]
169, 321, 585, 1040	-	Power density $< 50 W L^{-1}$ , the yields of $\cdot OH$ radical: $585 > 321 > 1040 > 169$ kHz. Power density $> 50 W L^{-1}$ , the yields of $\cdot OH$ radical: $585 > 1040 > 321 > 169$ kHz. While the yield of $H_2O_2$ reaches a maximum value in the vicinity of 300 kHz.	Mark, 1998	[121]
205, 358, 618, 1078	-	$H_2O_2$ is clearly highest at 358 kHz and lowest at 1078 kHz.	Kang, 1999	[107]

\* Only first author is listed.

Table 2-4 *Effects of frequency on decomposition rates of organic solutes*

Frequency*	Organic solutes	Decomposition rates of organic solutes	Authors**	References
20, 500	benzene, chlorobenzene, phenol, and chlorophenol	It is high at 500 and low at 20 kHz.	Lamy, 1993	[60]
20, 500	phenol	The degradation is faster at 500 than at 20 kHz with the identical acoustical power (30 W).	Petrier, 1994	[90]
20, 500	4-nitrophenol	It is faster at 500 than at 20 kHz.	Barbier 1996	[100]
20, 520	trichloroethylene	The degradation is energetically more efficient at 520 kHz.	Drijvers, 1996	[76]
20, 200, 500, 800	phenol and carbon tetrachloride	The degradation rate for CCl <sub>4</sub> increases with the frequency. Phenol degradation has a maximum value at 200 kHz.	Petrier, 1997	[119, 120]
20, 900	220 ppm chlorobenzene	Chloride formation rate at 20 kHz is significantly less than the rate at 900 kHz with the same ultrasonic power.	Kruus, 1997	[82]
20 ~ 1078	tetrachloromethane and hexachloroethane	The rates of degradation increase with increasing frequency with optimal degradation rates at 500 kHz.	Hung, 1999	[71]
205, 358, 618, 1078	methyl tertiary butyl ether (MTBE)	The higher reaction rates are observed at 358 and 618 kHz with identical power density.	Kang, 1999	[107]
205, 358, 618, 1078	Chlorinated hydrocarbons	The rate constants of the sonochemical degradation increased with frequency up to 600 kHz, and then declined.	Calussi, 1999	[122]
200 ~ 1045; 400 ~ 850; 534 ~ 2864	MTBE	Ranging from 200 to 620 kHz, the sonolytic rate is nearly independent on the frequency. Above 620 kHz, the effectiveness drops. The sonolysis is practically independent of the frequency in the range of 400 ~ 850 kHz. The effectiveness drops with increasing frequency in the range of 534 ~ 2864 kHz..	Lifka, 2000	[113]

\* Unit: kHz; \*\* Only first author is listed.

### 2.5.3 Effects of Acoustic Power

Acoustic intensity and acoustic power density are usually used to express the acoustic power. Acoustic intensity ( $W\ cm^{-2}$ ) is the acoustic power per unit area of transducer tip. Acoustic power density ( $W\ L^{-1}$ ) is the acoustic power per unit volume of solution.

Acoustic power has a dramatic influence on the rates of sonochemical reactions. In general, an increase in power density results in an increase in the observed sonochemical reaction rate. However, it is often observed experimentally that as one continues to increase the acoustic amplitude, rates begin to diminish eventually [7, 123].

The cavitation bubble size, the bubble collapse time, the transient temperature, and the internal pressure in the cavitation bubble during the collapse are all dependent on the power intensity. For example, the power intensity, which is proportional to the applied power density, is a function of the acoustic amplitude ( $P_A$ : bar) as below:

$$I = P_A^2 / 2\rho c \quad (E\ 2-6)$$

where  $I$  is the acoustic intensity ( $\text{W cm}^{-2}$ ),  $\rho$  is the density of the medium, and  $c$  is the velocity of sound in the medium.

For the aqueous solution [123],

$$I = 0.34P_A^2 \quad (E\ 2-7)$$

For a cavitation bubble, the maximum bubble size is dependent on the density of the liquid, the applied frequency, the hydrostatic pressure, and the acoustic pressure as follows [124]:

$$R_{\max} = \frac{4}{3\omega_a} (P_A - P_h) \left( \frac{2}{\rho P_A} \right)^{1/2} \left[ 1 + \frac{2}{3P_h} (P_A - P_h) \right]^{1/3} \quad (E\ 2-8)$$

where  $\omega_a$  is the applied acoustic frequency and  $P_h$  is the external pressure (usually,  $P_h = 1$  atm).

In addition, the bubble collapsing time ( $\tau$ ), is proportional to the maximum bubble size,  $R_{\max}$ :

$$\tau = 0.915 R_{\max} (\rho / P_m)^{1/2} \left( 1 + \frac{P_v}{P_m} \right) \quad (E\ 2-9)$$

where  $P_m$  is the pressure in the liquid (i.e.,  $P_m = P_h + P_A$ ) and  $P_v$  is the vapor pressure in the bubble.

Therefore, at high acoustic intensity (i.e., large  $P_A$  values), the cavitation bubbles are able to grow larger in size during a rarefaction cycle such that insufficient time is available for complete collapse during a single compression cycle. Thus, there is an optimum power, which can be applied during sonochemical irradiation in order to obtain maximum reaction rates.

Weissler et al. [19] investigated the effect of the volumes of KI solutions (i.e. power density) on the sonolytic yield of iodine with a constant power. Increasing the volume of a KI solution caused a rapid initial increase in iodine yield up to a maximum at about 200 mL, and then a gradual decrease at larger volumes. Thus, there is an optimum power density. Furthermore, when all other conditions are kept constant, increasing the power input leads the increase of yields almost linearly if the volume of solution is large enough (200 mL). However, for the smaller volumes (20 or 50 mL), the yield first increases and then decreases sharply. This shows again that there is an optimum power density.

The effects of ultrasonic power on sonochemical reaction rates in aqueous solutions are summarized in Table 2-5. Based on Table 2-5, the rate increases with an increase in power density. Moreover, a large horn tip produces more bubbles as it contacts a larger surface area of the liquid, and a lower intensity (larger tip area) results in more efficient sonochemical reaction [30].

Table 2-5 Effects of ultrasonic powers on sonochemical reaction rates in aqueous solutions

Reactions	Ultrasonic power	Other conditions	Reaction rates	Authors*	Reference
Oxidation of KI in water	With the same acoustic power	20 kHz	The greater the area of horn tip, the greater the rate of oxidation.	Entezari, 1996	[116]
Production of H <sub>2</sub> O <sub>2</sub>	10-50 W cm <sup>-2</sup>	-	The rate constant linearly increases with the increase of intensity at low intensities, but the increase slows at higher intensities. The optimum intensity is about 40 W cm <sup>-2</sup> .	Price, 1993	[125]
	-	-	Increases with increasing ultrasound power absorbed, finally to flatten out.	Mark, 1998	[121]
	100-240 W L <sup>-1</sup>	-	It is about twice at 240 than at 100 W L <sup>-1</sup> .	Kang, 1999	[107]
Decomposition of organic solutes	0.98-7.27 W mL <sup>-3</sup>	p-nitrophenol	The pseudo-first-order rate constant increases proportionally from $1.00 \times 10^{-4}$ to $7.94 \times 10^{-4} \text{S}^{-1}$ with increasing power density. Increase in k up to a maximum value of $8.6 \times 10^{-4} \text{S}^{-1}$ at a power intensity of 1.2 W cm <sup>2</sup> .	Hua, 1995	[102]
	the same acoustic power	20 KHz, chlorobenzene	The larger tip area (lower intensity), the more efficiently conversion of organic chlorine into chloride.	Kruus, 1997	[82]
	50-240 W L <sup>-1</sup>	205 and 358 kHz, MTBE	The rate constant increases rapidly with an increase in power density up to 240 W L <sup>-1</sup> .	Kang, 1999	[107]
	30-200 W 5 W cm <sup>-2</sup>	353 kHz, 25 mgL <sup>-1</sup> MTBE, 0.5 L, 293 K	Below 100 W, the rate constant rises linearly with the ultrasonic power. Above 166 W, the sonolytic rate of MTBE does not increase.	Lifka, 2000	[113]

\* Only first author is listed.

#### 2.5.4 Effects of the Bulk Liquid Temperature and Applied Pressure

The liquid temperature and applied pressure dramatically affect the sonochemical reaction rates. The bulk temperature and static pressure first affect the vapor pressure, gas solubility, components in cavities, and thermal activation. Thereby, the intensity of collapse and the secondary reaction rate are influenced [7].

On the one hand, the effective maximum temperature generated during the cavitation collapse is inversely proportional to the vapor pressure (*E2-1*). A bubble contains not only the gas that is dissolved in the liquid, but also vapor from the liquid itself. The amount of vapor in the bubble depends on the vapor pressure of the liquid, which is strongly dependent on the temperature of the bulk liquid. Higher temperature and lower applied pressure lead to an increase of the vapor pressure of the solvent; thereby the efficiency of the collapse of cavity decreases. The degree of heating of the bubble contents will be less since the proportion of water vapor increases with increasing temperature (e.g. < 1% at < 283 K and 30% at 343 K) and therefore the value of  $\gamma$



( $C_p/C_v$ ) of the gas-vapor mixture decreases. Furthermore, increasing temperature decreases the surface tension and decreases the collapse temperature of cavities [9, 121].

On the other hand, the increasing amount of water vapor in the bubble can promote the formation of free radicals from the dissociation of water molecules [126]. In addition, the rates of the subsequent reactions should increase with an increase in temperature [116]. Therefore, when the subsequent radical reaction plays an important role, increasing liquid temperature can favor the sonochemical reaction.

In conclusion, the rate of the homogeneous sonochemical reaction decreases as the bulk temperature is increased [9], but some exceptional cases exist. Table 2-6 shows the effects of the bulk liquid temperature on sonochemical reaction rates in aqueous solutions.

A limiting applied pressure exists for the formation of cavities. Over the limiting pressure, the nucleation of cavities can no longer occur, since the acoustic field must overcome the combined tensile strength of the liquid and the ambient pressure. In contrast, reducing the ambient pressure can also diminish the observed sonochemistry [7]. At room temperature, a sonolysis is carried out under the reduced external pressure, the sonochemical activity effectively ceases when the external pressure is below 0.1 atm [121].

Table 2-6 *Effects of liquid temperature on sonochemical reaction rates in aqueous solutions*

Reactions	Bulk liquid temperature range [°C]	Other conditions	Reaction rates	Authors*	Ref.
Oxidation of KI in water	-	-	Higher temperatures give smaller yields.	Weissler, 1950	[19]
	-	20 and 900 kHz	At 20 kHz, the rate of oxidation decreases with increasing temperature. At 900 kHz, the rate of oxidation can increase with temperature, up to 303 K.	Entezari, 1996	[116]
H <sub>2</sub> O <sub>2</sub> and ·OH radical formation	20, 40	-	It is over twice higher at 315 K than that at 293 K.	Spurlock, 1970	[26]
	17 ~ 57	-	At 305 K the yield of ·H radicals reaches maximum value, and at 320 K the yield of ·OH radical reaches maximum value.	Sochard, 1997	[126]
	10 ~ 70	-	The free-radical yield decreases over 50% when the aqueous temperature increase from 283 K to 343 K.	Mark, 1998	[121]
Decomposition rates of organic solutes	5, 15, 25, 35	353 kHz, 100 W, 500 mL, 25 mg L <sup>-1</sup> MTBE	Degradation rates increase with increase of temperature, but over 298 K, no significant increase of the rate by further temperature rise.	Lifka, 2002	[109]

\* Only first author is listed.

### 2.5.5 Effects of the Dissolved Gas

Earlier investigators have extensively stated that dissolved gases are essential for the sonochemical reaction. In 1950, Griffing noted that the rate of the hydrolysis of  $\text{CCl}_4$  is strongly dependent on the  $\gamma$  of the dissolved gas [65]. Weessler et al. [19] confirmed the effect of dissolved gases ( $\text{O}_2$ ,  $\text{N}_2$ , He,  $\text{CO}_2$ , vacuum) on the iodine yields during the ultrasonic irradiation of KI solutions in the absence of  $\text{CCl}_4$  and with a large excess of  $\text{CCl}_4$ . If the solution is saturated by  $\text{CO}_2$  or degassed by boiling under vacuum for 10 minutes, no iodine is produced upon irradiation, either with or without  $\text{CCl}_4$ . The effect of  $\text{N}_2$  and  $\text{O}_2$  on the iodine yield is the same as for air without  $\text{CCl}_4$ . This indicates that dissolved  $\text{O}_2$  is not essential for the iodine production. However, the iodine yield is larger under  $\text{O}_2$  than that under  $\text{N}_2$  in the presence of  $\text{CCl}_4$ . An interesting case is that no iodine at all is produced in  $\text{CCl}_4$ -free and He-saturated solutions, but in the presence of an excess of  $\text{CCl}_4$ , as much iodine is produced as in air-saturated solutions. Therefore, in order to facilitate cavitation, at least a dissolved gas must be present.

There are three reasons for the strong effects of the dissolved gases on the sonochemical reactions. Firstly, the temperature inside the collapsing bubble is in close relationship with the ratio of specific heat ( $C_p/C_v$ ) of the gas ( $E2-I$ ) [9, 27, 127]. Secondly, the dissolved gases with low thermal conductivity (e.g., Ar) favor high collapse temperatures and produce greater sonochemical yields than those with high conductivity, because the heat of collapse will dissipate less quickly from the cavitation site [28, 121]. Thirdly, highly soluble gases result in the formation of a larger number of cavitation nuclei and more extensive bubble collapse, since gases with higher solubility are more readily forced back into the aqueous phase. Therefore, a gas with high ratio of specific heat, low thermal conductivity, and high water solubility should yield the highest temperature during the cavitation bubble collapse.

In fact, the effective temperatures of collapsing bubbles during the sonolytic degradation of p-nitrophenol were estimated as follows: 779 K under Kr, 772 K under Ar, and 750 K with He [56]. Moreover, thermal conductivities of the dissolved gases have also been inversely correlated to sonoluminescence intensity [28, 128], as well as with variable rates of free-radical formation during sonolyses [129]. Makino et al. [130] used the method of spin trapping with radicals scavengers combined with EPR for the detection of  $\cdot\text{OH}$  and  $\cdot\text{H}$  radicals. EPR signal intensity of the OH-DMPO and the H-POBN adducts showed that sonolytic yields of  $\cdot\text{OH}$  and H radicals are larger with Ar than with  $\text{N}_2$ .

Table 2-7 shows the polytropic index, thermal conductivity, and water solubility of gases, which usually are filled in sonochemical reactions. Table 2-8 shows effects of dissolved gases on sonochemical reaction rates.

## 2.5 Sonochemistry of Organic Compounds in Aqueous Solutions

Table 2-7 Physical properties of the selected gases used during the sonolysis

Gas	Ratio of specific heat $\gamma = c_p/c_v$	Thermal conductivity $\lambda$ (mW mK <sup>-1</sup> )	Water solubility, $S_W$ (m <sup>3</sup> m <sup>-3</sup> /0.1 MPa, 288 K)
Water		47.1	-
Air	1.40*	45.7	-
O <sub>2</sub>	1.49 (380 K), 1.40*	36.1 (380 K)	$2.756 \times 10^{-5}$
N <sub>2</sub>	1.41, 1.41*	47.4	$1.386 \times 10^{-5}$
CO <sub>2</sub>	1.30*	41.6	$8.210 \times 10^{-4}$
Kr	1.66	17.1	$5.696 \times 10^{-5}$
Ar	1.82 (380 K), 1.67*	24.9 (380 K)	$3.025 \times 10^{-5}$
He	1.66, 1.66*	252.4	$7.123 \times 10^{-6}$
CH <sub>4</sub>	1.32*	88.3	$3.122 \times 10^{-5}$
C <sub>2</sub> H <sub>6</sub>	1.22*	70.5	$4.556 \times 10^{-5}$
C <sub>3</sub> H <sub>8</sub>	1.15*	-	-
C <sub>4</sub> H <sub>10</sub>	1.11*	-	-
C <sub>5</sub> H <sub>12</sub>	1.06*	-	-

C<sub>p</sub>: isobaric heat capacity; C<sub>v</sub>: isochoric heat capacity

Sources: David R. Lied CRC Handbook of Chemistry and Physics, 83<sup>rd</sup> (at 10 MPa, 600 K ratio of specific heat and thermal conductivity, p 6-17, 193; Water solubility, p 8-86) [131].

\*Mark's Standard Handbook for Mechanical Engineers, 9th ed., (at 0.1 MPa, 293 K) [132].

Table 2-8 Effects of dissolved gases on sonochemical reaction rates in aqueous solutions

Reactions	Dissolved gases	Other conditions	Reaction rates	Authors*	Reference
Oxidation of KI solution	O <sub>2</sub> , Ar	20 and 514 kHz	Rates of formation for I <sub>3</sub> <sup>-</sup> and H <sub>2</sub> O <sub>2</sub> : at 20 kHz, Ar > O <sub>2</sub> ; at 514 kHz, O <sub>2</sub> > Ar.	Petrier, 1992	[117]
	Ar, air	20 and 900 kHz	Rate of oxidation: At 20 kHz, Ar > air; At 900 kHz, air > Ar.	Entezari, 1996	[116]
Formation of H <sub>2</sub> O <sub>2</sub> and ·OH radical	O <sub>2</sub> , Ar		Yield of H <sub>2</sub> O <sub>2</sub> : O <sub>2</sub> > Ar	Weissler, 1959	[16]
	O <sub>2</sub> , Ar, Ne, He, N <sub>2</sub>	800 kHz, 9.4 W cm <sup>-2</sup> , at 293 K and pH 7.0	Rates of H <sub>2</sub> O <sub>2</sub> formation: O <sub>2</sub> > Ar > Ne > He > N <sub>2</sub> .	Spurlock, 1970	[26]
	O <sub>2</sub> , Ar, Kr, He	20, 40, 80, 500 kHz	Rate constants for the yield of H <sub>2</sub> O <sub>2</sub> and ·OH radical: Kr > Ar > O <sub>2</sub> > He.	Hua, 1997	[18]
	O <sub>2</sub> , Ar, Air, He	321 kHz, 170 W L <sup>-1</sup>	Yields of H <sub>2</sub> O <sub>2</sub> from pure water and ·OH radical: Ar > O <sub>2</sub> > Air > He	Mark, 1998	[121]
	O <sub>2</sub>	205 kHz, 244 W L <sup>-1</sup>	Apparent H <sub>2</sub> O <sub>2</sub> production rates under Ar and O <sub>2</sub> are identical.	Kang, 1999	[107]
Composition rates of organic solutes	O <sub>2</sub> , Ar	pentachlorophenolate	Degradation rate: Ar > O <sub>2</sub> and air.	Petrier, 1992	[133]
	O <sub>2</sub> , Ar	p-nitrophenol	Rate constant for degradation: Ar > O <sub>2</sub> ; A 4:1 (v/v) Ar/O <sub>2</sub> mixture yields the highest degradation rate.	Hua, 1995	[102]
	Kr, Ar, He	p-nitrophenyl acetate	Pseudo first-order-rate constant: Kr > Ar > He.	Hua, 1995	[56]
	Air, Ar	chlorobenzene	Degradation rate: Ar > air.	Drijvers, 1998	[80]

\* Only first author is listed.

In conclusion, the presence of other polyatomic volatile components, the solution will depress the value of the ratio of specific heat below that of a pure monoatomic or diatomic gas [121]. In some cases, the reaction with gases such as O<sub>2</sub> is directly affected by the high temperature during the collapse of the bubble. They are able to undergo reactions with products of water sonolysis. As a

consequence, reactive species available and the rate of production will depend on the nature of the gas [116, 133].

### 2.5.6 Effects of Organic Solutes

The physicochemical properties, such as hydrophobicity, volatility, initial concentration, thermostability, and reactivity of organic solutes can affect their sonochemical behavior. In 1950, Weissler et al. [19] investigated the effect of the amount of  $\text{CCl}_4$  (0.01 – 10 mL) on the sonolytic yield of iodine in 20 mL KI solution. They found that 0.01 mL  $\text{CCl}_4$  is optimum, and larger amounts of  $\text{CCl}_4$  cause excessive scattering of the ultrasonic energy and therefore lower yields. Reifsneider et al. [33] demonstrated that the relative proportions of products ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_6$ ) depended most strongly on the functional groups and to a lesser extent on the length and structure of the carbon chain during ultrasonic irradiation of aliphatic aldehydes and carboxylic acids in an aqueous medium. Two reaction pathways exist for the aldehydes (i.e., oxidation to the corresponding carboxylic acid and fragmentation to smaller carboxylic acids with concurrent formation of the  $\text{C}_1$  and  $\text{C}_2$  gases). For carboxylic acids only the latter process is available.

Henglein et al. [34] discovered the efficiency of  $\cdot\text{OH}$  radical scavenging is correlated to the hydrophobicity of solutes during aqueous sonolyses. The higher hydrophobicity increases the capacity of the solute for trapping  $\cdot\text{OH}$  radicals. However, the vapor pressure of the scavenger is not the determining factor. Effects are explained in terms of  $\cdot\text{OH}$  radical formation in gaseous bubbles, combination of  $\cdot\text{OH}$  radicals to form  $\text{H}_2\text{O}_2$  at the interfacial area, and enrichment of hydrophobic solutes in the bubbles. Also, solutes suffer pyrolytic degradations [134].

As a cavitation bubble collapses, the gas inside is compressed almost adiabatically. The temperature rise depends upon the specific heat of the gas mixture. The specific heat  $C_p$  of vapors of aromatic compounds is  $120 \text{ J mol}^{-1} \text{ K}^{-1}$ , and much higher than the specific heat of air ( $30 \text{ J mol}^{-1} \text{ K}^{-1}$ ) or water vapor ( $36 \text{ J mol}^{-1} \text{ K}^{-1}$ ). Therefore, the adiabatic temperature rise upon compression of a cavitation is much lower if an aromatic vapor is present. Excessive amounts of aromatic compounds lower the temperature of a collapse cavitation bubble, which lowers the rate of degradation [63, 77, 78, 135]. Similarly, the average temperatures in the reaction zone during the sonolysis of p-nitrophenol were evaluated [35]. The temperature of the interfacial region was found to vary between  $T = 740$  and  $790 \text{ K}$ . The temperature decreases with the increase of the initial concentration of p-nitrophenol.

Ashokkumar et al. [136-138] observed the effects of organic solutes on multi-bubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) in water. Low

concentrations of short chain aliphatic alcohols and organic acids and bases suppress MBSL and SBSL in water. The intensity of the emitted light decreases with increasing concentrations of alcohols, and the extent of quenching increases as the length of the alkyl chains of alcohols increases. Butyric acid and propylamine behave in the same manner, but only in their neutral forms, indicating that the SBSL suppression is due to processes occurring within the bubble.

Didenko et al. [53] analyzed excited-state C<sub>2</sub> MBSL spectra from dilute aqueous solutions of pentane, cyclohexane, benzene, ethanol, t-butyl alcohol, and acetone in water at 20 kHz. All substrates led to a weak C<sub>2</sub> emission and a significant decrease in the SL intensity of water. In addition, the intensity of SL decreases across the entire spectral region as the concentration of benzene (0.01 ~ 0.08 %) increases, and the effective emission temperature was estimated as 4300 ± 200 K by analyzing the MBSL spectrum of 0.01% benzene in water at 278 K under Ar.

The Henry's Law constant might be strongly associated with the solute transfer rate from the bulk media to the cavity during the sonochemical destruction of trichloroethylene, tetrachloroethylene, benzene and toluene [79]. In addition, a higher vapor pressure results in more solutes diffusing into the bubbles and undergoing pyrolytic decomposition as the bubbles collapse [71, 122].

Table 2-9 shows the effects of organic solutes on sonochemical reactions.

Table 2-9 Effects of organic solutes on sonochemical reactions in aqueous solutions

Reactions	Organic solutes	Other conditions	Reaction rates	Authors*	Ref.
Oxidation of KI in water	0.01 – 10 mL tetrachloromethane	20 mL KI solution	0.01 mL CCl <sub>4</sub> is optimum.	Weissler, 1950	[19]
Formation of H <sub>2</sub> O <sub>2</sub> and ·OH radical	-	-	Efficiency of ·OH radical scavenging is correlated to the hydrophobicity of the solutes, but vapor pressure of the scavenger is not the determining factor.	Henglein, 1985	[57]
Decomposition of organic solutes	p-nitrophenol	24 kHz, 3360 W L <sup>-1</sup> , effect of initial concentration	The first-order degradation rate constant decreased from $1.37 \times 10^{-2}$ to $6.17 \times 10^{-5}$ S <sup>-1</sup> as the concentration of p-nitrophenol increased from 0.01 to 1.0 mmolL <sup>-1</sup> .	Kotronarou, 1991	[35]
	benzene, chlorobenzene, phenol, and chlorophenol	500 kHz	Benzene and chlorobenzene disappeared faster than phenol and chlorophenol.	Lamy, 1993	[60]
	benzene, ethylbenzene, styrene, and o-chlorotoluene	various initial concentrations in the millimole range	Reaction rates are higher at low concentrations.	Visscher, 1996	[135]
	MTBE	205 kHz, 200 W L <sup>-1</sup> , effect of initial substrate concentration	The first-order degradation rate constant decreased from $8.5 \times 10^{-4}$ to $4.1 \times 10^{-4}$ S <sup>-1</sup> as the concentration of MTBE increased from 0.01 to 1.0 mmolL <sup>-1</sup> .	Kang, 1998	[36]
	trichloroethylene and chlorobenzene	effect of the initial concentration at millimole concentration ranges	At higher concentrations, slower sonolytic rates are obtained.	Drijvers, 1999	[77]
	tetrachloromethane, trichloromethane, dichloromethane	205 kHz and 50 W, Henry's law constant	The order of degradation is CCl <sub>4</sub> > CHCl <sub>3</sub> > CH <sub>2</sub> Cl <sub>2</sub> .	Hung, 1999	[71]
	chlorinated hydrocarbons	205, 358, 618, and 1078 kHz, Henry's Law constant	The rate constants of the sonochemical degradation at all frequencies increased with Henry's Law constant.	Calussi, 1999	[122]
	MTBE	The influence of initial concentration (ranging 2 to 200 mg L <sup>-1</sup> )	The degradation rate of MTBE decreases with the increase of initial concentration.	Lifka, 2000	[113]
	trichloroethylene and chlorobenzene	At micromole concentration ranges	Higher initial concentrations of organic solutes result in lower collapse temperatures and degradation rates.	Dewulf, 2001	[78]
trichloroethylene, tetrachloroethylene, benzene and toluene	The effect of Henry's Law constant and the initial concentration.	Decay rate of trichloroethylene is the greatest. The rate constants of trichloroethylene decreases with the increase of the initial concentration of trichloroethylene to the level of 200 μM, but the stays constant increasing the initial concentration of trichloroethylene further.	Kang, 2001	[79]	

\* Only first author is listed.

### 2.5.7 Effects of pH Values of the Solutions

The pH value of the solution directly influences the volatility and reactivity of organic solutes, thereby affects the sonochemical behavior of organic solutes, especially the solutes with  $-OH$ ,  $-NH_2$ , and  $-COOH$  groups.

The effect of pH value on the ultrasonic cleavage of phenol and pyridine was investigated in 1962 [32]. The ultrasonic cleavage of the ring to produce acetylene is only barely detectable when pyridine is converted into the pyridinium salt in acid solution, and when phenol is converted into sodium phenoxide in basic solution.

Kotronarou et al. [35] investigated the influence of the changes in the initial pH of the p-nitrophenol (PNP) solutions on the decay of PNP. PNP decayed exponentially with time at all pH values. The pseudo-first-order rate constant decreased with the increase of pH (pH = 5 to 8), and remained constant up to pH = 10. At pH > 10 the pseudo-first-order rate constant increased slightly because of the slow thermal reaction between PNP and  $\cdot OH$  radical/ $H_2O_2$ .

Sperpone et al. [139] investigated the sonochemical oxidation of phenol in air-equilibrated aqueous media at various pH values and at various ultrasonic powers. Three principal intermediate species formed at pH = 3: catechol, hydroquinone, and p-benzoquinone; at pH = 5.4 – 5.7 only catechol and hydroquinone formed. No intermediate species were detected at pH = 12. Furthermore, at pH = 3, p-benzoquinone is the major species formed during the sonication of hydroquinone, while hydroquinone is produced during the sonication of p-benzoquinone. It is argued that the hydrophobic benzoquinone reacted with  $\cdot OH$  and  $\cdot H$  radicals at the hydrophobic gas bubble/liquid interface, while the hydrophilic species (phenol, catechol, and hydroquinone) reacted, to a large extent, with the  $\cdot OH$  radicals in the bulk solution.

Furthermore, Drijvers et al. [76] found that the degradation of trichloroethylene is fastest in basic solutions. However, no influence of the pH value of the aqueous solutions on the sonolysis of chlorobenzene was found [80].

In conclusion, the formation of salts reduces the vapor pressure of the reactants to such an extent that they are unable to enter the bubbles present and are, hence, unaffected by the ultrasonic waves [32].

## 2.6 Sonochemistry of Organic Chemicals in Nonaqueous Liquids

Since the ultrasonic decolorization of DPPH radical in methanol was reported in 1953, only little investigations dealt with the ultrasonic irradiation of organic liquids and the sonochemistry of solutes dissolved in organic liquids [7, 8]. In 1965, Weissler et al. [140] investigated sonolyses of  $\text{CH}_3\text{CN}$  and  $\text{CCl}_4$ .  $\text{CH}_3\text{CN}$  gave small amount of  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ ;  $\text{CCl}_4$  gave  $\text{Cl}_2$ . Hence cavitation effects may occur in organic liquids.

Sonochemistry cannot be observed in most common volatile organic solvents, since many organic liquids have high vapor pressures, which greatly diminish the intensity of the, cavitation collapse. It has been demonstrated that the single-bubble sonoluminescence (SBSL) emitted from organic liquids (mostly alcohols) are weaker than that from water, e.g., n-butanol in air apparently gives a very weak emission about 200 times less intense than water [141].

However, the ultrasonic irradiation can always bring about the secondary reactions in aqueous solutions. It is difficult to interpret the complexity of the secondary reaction. In order to avoid such difficulties, the sonochemistry of organic liquids should be investigated. As long as the liquid temperature is sufficiently low (sufficiently low vapor pressure), in principle, all organic liquids undergo cavitation and generate bond homolysis [7, 29]. The sonochemistry of organic liquids is summarized in Table 2-10.

Table 2-10 *Nonaqueous sonochemistry of organic compounds*

	Substrates	Intermediates and products	Authors*	Ref.
N-compound	acetonitrile	$\text{H}_2$ , $\text{CH}_4$ , $\text{N}_2$	Weissler, 1965	[140]
Halogenated aliphatic hydrocarbons	tetrachloromethane	$\text{Cl}_2$ , $\text{C}_2\text{Cl}_6$	Weissler, 1965	[140]
	trichloromethane	$\text{HCl}$ , $\text{CCl}_4$ , $\text{CH}_2\text{Cl}_2$ , $\text{C}_2\text{Cl}_5\text{H}$ , $\text{C}_2\text{Cl}_4$ , $\text{C}_2\text{Cl}_6$ , $\text{C}_2\text{HCl}_3$	Suslick, 1983	[40]
	bromo-trichloromethane	$\text{Cl}_3\text{CCCl}_3$ and $\text{Br}_2$	Kimura, 1998	[142]
Aliphatic hydrocarbons	alkanes	$\text{H}_2$ , $\text{CH}_4$ , $\text{C}_2\text{H}_2$ , 1-alkenes	Suslick, 1983	[41]
	alkanes	$\text{H}_2$ , $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , 1-alkenes	Mizukoshi, 1999	[43]
	n-dodecane ( $\text{C}_{12}$ )	$\text{C}_7$ , $\text{C}_8$ , $\text{C}_9$ , $\text{C}_{10}$ components	Price, 1995	[143]
	diesel fuel	Insoluble sediment (Polymers involving N-containing and other aromatic components)	Price, 1995	[143]
	decalin	$\text{H}_2$ , tetralin, naphthalene, o-xylene, ethylene	Cataldo, 2000	[144]
	teralin	$\text{H}_2$ , naphthalene,	Cataldo, 2000	[144]
Aromatic hydrocarbons	benzene	acetylene, $\text{H}_2$ , biphenyl, methane toluene	Suslick, 1988	[7]
	benzene	carbon fine particles	Katoh, 1998	[145]
	benzene	polymerization products	Katoh, 1998	[146]
	benzene	150 mL of liquid benzene for 1 h (600 W, 20 kHz), approximately 1 $\mu\text{g}$ of $\text{C}_{60}$	Katoh, 1998	[147]
	benzene, toluene	$\text{H}_2$ , $\text{CH}_4$ , $\text{C}_2\text{H}_2$ , toluene, biphenyl, poly-p-phenylene, polyvinylbenzene, polystyrene, coke	Cataldo, 2000	[144]
	toluene	$\text{H}_2$ , $\text{CH}_4$ , benzene, xylenes and 1,2-diphenylethane	Suslick, 1988	[7]
Alcohols	alcohols	$\text{H}_2$ , $\text{CO}$ , $\text{CH}_4$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , aldehydes	Mizukoshi, 1999	[43]

\* Only first author is listed.



The property of a liquid has a profound influence over the observed sonochemistry as well. The vapor pressure is the principal determinant of the conditions formed during cavitation (*E2-1*). Surface tension and viscosity can alter the threshold of cavitation, but they are generally a minor concern. In addition, the chemical reactivity of the liquid is often important [7].

### 2.6.1 Roles of Vapor Pressures of Organic Liquids

Suslick et al. [41] reported the sonochemistry of alkanes in 1983. They illustrated that a decreasing vapor pressure of the solvent increases the intensity of cavitation collapse, the maximum temperature of the collapse, and the rates of sonochemical reactions. Primary products are H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and smaller 1-alkenes. Mizukoshi et al. [43] reported the effect of the vapor pressure and evaporation on sonolyses of organic liquids in 1999. Hydrocarbons most efficiently decomposed under the vapor pressure range of 0.1-0.5 Torr, while the most efficient vapor pressure for sonolyses of alcohols is about 15 Torr. On the one hand, a higher vapor pressure leads to less formation of cavities and lower efficiency of collapse. On the other hand, the higher vapor pressure lowers the ratio of specific heats ( $\gamma$ ) of gases in cavitation bubbles, since the  $\gamma$  values of organic liquids are generally low (e.g.  $\gamma = 1.67$  for Ar and about 1.0-1.3 for general organic vapors (Table 2-7)). The main products are H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> from hydrocarbons, and H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO and aldehydes from alcohols. Katoh et al. [146] studied the sonochemical polymerizations of benzene and halogen-substituted benzenes in 1998. The relative rate constant of the polymerization reaction is apparently proportional to the inverse of the vapor pressure of the liquid. The trend of the darkening of the absorption spectrum has the following order: Ph-F > Ph-Cl > Ph-Br > Ph-H.

Therefore, decreasing the vapor pressure is always favorable for sonolyses of organic liquids.

### 2.6.2 Ultrasonic Cleavage of Organic Liquids and Radical Reactions

Suslick et al. [41] discovered that sonolyses of alkanes (under Ar at 298 K) is quite similar to very high temperature pyrolysis, and hydrogen, methane, 1-alkenes are the principal products. The principal products from the sonolysis of benzene are hydrogen, methane, toluene, and biphenyl. The products distribution from toluene, o-xylene, and mesitylene is similar [7].

Misik et al. [148, 149] investigated sonolyses of n-alkanes (C<sub>8</sub>-C<sub>16</sub>), n-alcohols (C<sub>3</sub>-C<sub>8</sub>), cyclohexane, toluene, dioxane, cyclic ethers, dimethylacetamide (DMA), and N, N-dimethylformamide (DMF) by EPR and spin trapping. 2,4,6-tri-*t*-butyl-nitrosobenzene (3tBNB) was found to be a particularly suitable spin trap since primary, secondary, and tertiary alkyl radicals could be distinguished. The reaction rate of nitrosodurene with C-centered radicals is

higher than that of 3tBNB. For a homologous series of n-alkanes and n-alcohols, the spin adduct yields increase markedly with the decreasing vapor pressure of the organic solvent. The nature of the radicals spin trapped is consistent with the Rice-Herzfeld pyrolytic mechanism. Radicals, produced by the pyrolysis in collapsing bubbles, such as  $\cdot\text{CH}_2\text{R}$  in n-alkanes,  $\cdot\text{CH}_2\text{R}$  and  $\cdot\text{CH}_2\text{OH}$  in n-alcohols,  $\cdot\text{CH}_2$ -phenyl in toluene,  $\cdot\text{CH}_2\text{OR}$  and  $\cdot\text{CH}_2\text{R}$  in cyclic ethers and  $\cdot\text{CH}_3$  and  $\cdot\text{N}(\text{CH}_3)\text{R}$  in DMF and DMA were spin trapped. Secondary radicals formed by hydrogen abstraction from organic liquids (such as  $\cdot\text{CHRR}'$  radicals in n-alcohols and n-alkanes and  $\cdot\text{CH}_2\text{N}$ -type radicals in DMF and DMA) by the primary pyrolysis radicals were also spin trapped. From the temperature dependence of the kinetic isotope effect, the temperature region of hydrogen abstraction radical formation ( $\cdot\text{CHRR}'$ ) in n-dodecane was estimated to be  $750 \pm 150$  K; the effective temperature of the region where benzyl radicals are formed from toluene by sonochemical pyrolysis was estimated to be about 6000 K.

The sonolysis of  $\text{BrCCl}_3$  in the presence and absence of 1-alkenes was performed by Kimura et al. [142]. In the absence of 1-alkene, dimer  $\text{Cl}_3\text{CCCl}_3$  and  $\text{Br}_2$  are products, and addition of the radical scavenger DPPH did not decrease the yield of the dimer. Thus, the fragmentation of  $\text{BrCCl}_3$  and the dimerization of radicals occur in the gas phase. In the presence of 1-octene, adducts were obtained, and DPPH sharply decreased the yields of adducts. Thus, radical chain reactions occur in the bulk liquid phase.

The ultrasound-induced cracking of some aromatic and naphthenic hydrocarbons are quite similar to very high temperature pyrolysis [144]. During the sonication of decalin and tetralin, dehydrogenation reactions occur. According to thermodynamic calculations, temperature as high as 773 K is necessary to achieve the same results. Benzene and toluene sonication causes aromatic ring breakdown with formation of acetylene and polymers. Acetylene formation from benzene is possible at 923 K with coke formation. Otherwise, temperature as high as 1973 K is needed. The sonolytic rate of toluene is higher than that of benzene, because toluene has a lower vapor pressure in comparison to benzene.

Recently, the decomposition of room-temperature ionic liquids was observed by Oxley et al. [150]. During the sonication, all of the imidazolium ionic liquids produced gases that contained trace amounts of light hydrocarbons, such as chlorobutane, chloromethane, benzene, toluene, and nitriles consistent with the decomposition of imidazoles.

### 2.6.3 Sonoluminescence and Temperatures at Hot Spots in Organic Liquids

The sonoluminescence (SL) spectra of dodecane (269 K,  $P_v = 0.006$  Torr), tetrachloroethylene (257 K,  $P_v = 1.3$  Torr), and nitroethane (254 K,  $P_v = 1.1$  Torr) under argon were observed by Suslick [14]. These sonoluminescence spectra demonstrate that ultrasound is a powerful chemical initiator and the significant chemistry occurs during ultrasonic irradiation even in the absence of reactive solutes. The total intensity of SL is strongly dependent on the vapor pressure of the solvent. This indicates that excited states are formed from cavitation collapse. The similarity between sonoluminescence and the chemiluminescence seen with other high-energy techniques (such as flames, plasmas, and shock tubes) indicates that similar chemistry is occurring during the ultrasonic irradiation of liquids.

Sonoluminescence spectra from silicone oil were reported in 1991, which was used to measure the temperatures reached in a cavitation bubble [52]. The observed emission came from excited state  $C_2$  (Swan band transitions). The effective cavitation temperature was found to be  $5075 \text{ K} \pm 156 \text{ K}$ . Sonoluminescence spectra from more volatile hydrocarbons did not give sufficient signals. In 1993, the sonoluminescence from the ultrasonic irradiation of organometallic compounds in silicone oil solutions were investigated [151]. Specifically, ultrasonic irradiation of solutions of  $0.01 \text{ M}$   $Fe(CO)_5$ ,  $Cr(CO)_6$ ,  $Mo(CO)_6$ , or  $W(CO)_6$  at  $268 \text{ K}$  produce atomic line emissions from metal atom excited states. Sonoluminescence produces localized hot spots with extreme temperatures and pressures and very short lifetimes.

In 1999, sonoluminescence was generated from  $2.5 \text{ mmol L}^{-1} Fe(CO)_5$ ,  $Cr(CO)_6$ , and  $0.25 \text{ mmol L}^{-1} Mo(CO)_6$  in poly(dimethylsiloxane) (Dow 200 silicone oil) irradiated at  $90 \text{ W cm}^{-2}$  at  $20 \text{ kHz}$  [25]. Fe, Cr, and Mo atom emission temperature are  $5100 \pm 300 \text{ K}$ ,  $4700 \pm 300 \text{ K}$ , and  $4800 \pm 400 \text{ K}$  under Ar respectively. The organic gas can affect the observed emission temperatures from MBSL. The measured emission temperatures for Ar mixtures with various hydrocarbons (methane, ethane, ethylene, and propane) are lower than for Ar only. Moreover, the temperatures decrease as the percentage of a given hydrocarbon is increased. The dissolved gas is Ar mixed with 0.0, 0.3, 1.0, 2.0, and 3.0 vol % propane in silicone oil with  $Cr(CO)_6$ , yielding respective emission temperatures of  $4700 \text{ K}$ ,  $3700 \text{ K}$ ,  $3400 \text{ K}$ ,  $3100 \text{ K}$ , and  $2500 \text{ K}$ . Similar results were observed for Fe with methane. Similarly, dissolved noble gases can also influence the observed emission temperatures from MBSL. The MBSL spectra are from solutions of  $Cr(CO)_6$  in octanol, the dissolved gases are Xe, Kr, Ar, Ne and He, with respective emission temperatures of  $5100 \text{ K}$ ,  $4400 \text{ K}$ ,  $4300 \text{ K}$ ,  $4100 \text{ K}$  and  $3800 \text{ K}$ . This indicates that the ratio of specific heat and the thermal conductivity play an important role. Moreover, an increase in the solvent vapor pressure is equivalent to increasing the percentage of hydrocarbon gas and leads to similar drops in

temperature. The MBSL spectra are from solutions of  $\text{Cr}(\text{CO})_6$  in octanol, vapor pressures are 0.007, 0.07 and 1.5 Torr, yielding emission temperatures of 4000 K, 3700 K, 3000 K and 2300 K, respectively.

Recently, the molecular emission from SBSL in polar aprotic liquids, including formamide ( $\text{H}_2\text{NCHO}$ ), N-methylformamide, N,N-dimethylformamide, N-methylacetamide, 1,2-diminoethane, dimethylsulfoxide, and adiponitrile were measured [152]. The emission intensities (relative to water at 1.0) are ordered as following: adiponitrile (2.0), formamide (1.2) methylformamide (0.14), dimethylsulfoxide (0.14), dimethylformamide (<0.05), and 1,2-diaminoethane (<0.05). Vapor pressure appears to be important for SBSL. Adiponitrile ( $P_v < 0.1$  Torr at 295 K) gives intense SBSL, whereas acetonitrile ( $P_v = 77$  Torr at 295 K), a liquid very similar in chemical properties to adiponitrile, fails to give any SBSL. Similarly, the intensity of SBSL decreases more than 20 times from formamide ( $P_v = 0.05$  Torr at 295 K) to methylformamide ( $P_v = 0.2$  Torr at 295 K), to dimethylformamide ( $P_v = 3.2$  Torr at 295 K). Moreover, the acoustic pressure during M-SBSL (moving single-bubble sonoluminescence) significantly affects the emission spectra. As  $P_A$  is increased during M-SBSL, the intensity of bubble collapse will also increase, leading to higher temperatures and an initial increase in CN emission, as more CN excited states are formed. As  $P_A$  is further increased, however, CN is either thermally dissociated or no longer formed within the collapsing bubble, and a sharp decrease in the intensity of CN emission was observed.

#### 2.6.4 Sonolytic Rates and Kinetics of Organic Liquids

DPPH is a well-known radical scavenger that would scavenge any radicals produced in sonolysis. The scavenging reaction may proceed at the interface region or in the bulk solution [41, 43, 142]. Thus, the rate of DPPH trapping in sonolysis is used to show both the formation of free radicals and the potential of the sonolysis of organic liquid.

Suslick et al. [41, 42] discovered that the bleaching rate of the radical scavenger DPPH decreases as the solvent vapor pressure increases. The results are consistent with the theory of hot spot. If the reaction mechanism in the bubble is governed by the Arrhenius equation (E2-5), in combination with the equation (E2-1) of the maximum temperature reached in reaction zones, the reaction rate constant ( $k$ ) decreases with increasing solvent vapor pressure ( $P_v$ ):

$$\ln k = \ln A - \frac{E_a}{RT} = \ln A - \frac{E_a}{RT_0 P_a (\gamma - 1)} \times P_v \quad (\text{E 2-10})$$

where  $A$  is the preexponential factor,  $E_a$  is the Arrhenius activation energy,  $T_0$  is the liquid temperature,  $R$  is the gas constant,  $P_a$  is the acoustic pressure at initiation of collapse,  $\gamma$  is the ratio of specific heats of dissolved gas or vapor.

Using the sonochemical kinetic data for ligand substitution of metal carbonyls in a mixture of two n-alkanes, in combination with the activation parameter ( $A$  and  $E_a$ ) from thermochemistry data, the effective temperatures of both sonochemical reaction sites have been experimentally estimated by Suslick et al. [47]. The effective temperature of the gas-phase reaction zone is  $5200 \pm 650$  K, and the liquid-phase effective temperature is about 1900 K. The efficacy of cavitation collapse and the temperatures generated are strongly dependent on the vapor pressure of the solvent system [40, 41]. Thus, the rate constant of  $\text{Fe}(\text{CO})_5$  decomposition decreases as the solvent vapor pressure increases. In addition, the rates of sonochemical ligand substitution are first order in metal carbonyl concentration [40].

The cavitation-induced polymerization of nitrobenzene with various organic solutes was investigated [153]. Liquids showed a marked darkening during the sonication. Dissolved gas and organic solutes can affect the rate of darkening of nitrobenzene. Hydrogen seems most effective in chemically inhibiting the polymerization, with  $\text{N}_2$ , He,  $\text{O}_2$ , and Ar in order of decreasing effectiveness. Hexane, methanol, ethanol, and acetone can also inhibit darkening. In the case of gaseous solutes, the major effect is gas solubility; in the case of liquid solutes, the major effects are the vapor pressure and the vapor heat capacity.

## 3 Experimental Part

### 3.1 Chemicals

The model chemicals were used as received from Fluka and Sigma-Aldrich. Their purities and physicochemical properties are listed in Table 3-1. Physicochemical data were taken from SRC PhysProp Database and NIST Chemistry Webbook [154-156].

Table 3-1 Properties of the model compounds and their purity

Groups	No.	Name	CAS	S <sub>w</sub> <sup>(a)</sup>	LogP <sub>ow</sub>	P <sub>v</sub> <sup>(b)</sup>	K <sub>H</sub> <sup>(c)</sup>	ΔH <sub>gas</sub> <sup>(d)</sup>	Purity <sup>(e)</sup>
Cyclic C <sub>6</sub> H <sub>x</sub>	1	benzene	71-43-2	1790	2.13	12.64	562.4	82.9	99.7
	2	1,4-cyclohexadiene	628-41-1	700	2.3	8.88	10537.8	104.8	98
	3	1,3-cyclohexadiene	592-57-4	295	2.47	12.97	8551.8	104.6	97
	4	cyclohexene	110-83-8	213	2.86	11.87	4610.3	-4.3	99.5
	5	cyclohexane	110-82-7	55	3.44	12.92	15198.8	-123.1	99
	6	methylcyclopentane	96-37-7	42	3.37	18.40	36781.0	-106.7	97
Aliphatic C <sub>6</sub> H <sub>x</sub>	1	2-hexyne	764-35-2	-	2.57	-	-	107.7	98
	2	3-hexyne	928-49-4	559	2.57	-	-	105.4	98
	3	1-hexyne	693-02-7	360	2.73	17.73	4042.9	-	97
	4	2,3-dimethyl-2-butene	563-79-1	71	3.19	16.80	59781.8	-70.3	97
	5	1,5-hexadiene	592-42-7	169	2.87	29.46	14286.8	85	97
	6	2,3-dimethyl-1-butene	563-78-0	78.5	3.13	33.60	42860.5	-65.9	99
Thiophenes	1	tetrahydrothiophene	110-01-0	3730	1.79	2.45	61.9	-33.6	97
	2	thiophene	110-02-1	3010	1.81	10.63	295.9	115	98
	3	2-methylthiophene	554-14-3	1210	2.33	3.32	327.3	84.4	97
	4	2,5-dimethylthiophene	638-02-8	352	2.91	1.31	361.7	-	98
	5	2-ethylthiophene	872-55-9	292	2.87	1.49	434.7	-	97
Thioethers	1	diethyl sulfide	352-93-2	3130	1.95	8.03	90.3	-82.7	98
	2	dipropyl sulfide	111-47-7	351	2.88	0.86	247.2		97
	3	dibutyl sulfide	544-40-1	39.4	3.87	0.16	435.7		98
	4	diallyl sulfide	592-88-1	621	2.61	1.23	136.8		95
	5	dipropyl disulfide	629-19-6	39.9	3.84	0.07	382.0	-117.3	97
	6	diethyl disulfide	110-81-6	300	2.86	0.57	217.8	-74.7	99
N-heterocycles	1	pyridine	110-86-1	1000000	0.65	2.77	1.1	140.7	99.8
	2	pyrrole	109-97-7	45000	0.75	1.11	1.8	108.3	97
	3	N-methylpyrrole	96-54-8	12100	1.21	2.85	19.7	103.1	98
Others		tetrachloroethene	127-18-4	206	3.4	2.47	1793.5	-12.43	99
		n-propanol	71-23-8	1000000	0.25	2.80	0.75	-255.6	99
		n-decane	124-18-5	0.052	5.01	0.19	386	-249.7	99
		styrene	100-42-5	310	2.95	0.85	278.6	146.9	99

Units: (a) mg L<sup>-1</sup>, (b) kPa, (c) kPa L mol<sup>-1</sup>, (d) kJ mol<sup>-1</sup>, (e) %.

## 3.2 Ultrasound Devices and Operating Conditions

All sonochemical experiments were conducted twice in parallel. The averages of the parallel experimental data were calculated and taken into account in analyses of sonochemical kinetics of the selected organic substrates. The error of all parallel experiments was under 5 %. In this section, the general operating conditions are stated. The special operating conditions are described in the corresponding sections.

### 3.2.1 Ultrasound Setup for Aqueous Solutions

The device consists of an ultrasonic power generator K 8 (Figure 3-1), an ultrasonic transducer E/805/T/02 and a double-walled cylindrical glass reactor (Figure 3-2) (Meinhardt Ultraschalltechnik, Leipzig). The structure and technological parameters of the ultrasonic device are detailed on the website of the manufactory [157].



Figure 3-1 Ultrasonic power generator K 8

Source: Meinhardt Ultraschalltechnik, Leipzig [157]



Figure 3-2 Ultrasonic transducer and a double-walled cylindrical glass reactor

Source: Meinhardt Ultraschalltechnik, Leipzig [157]

The scheme of the applied apparatus for ultrasonic irradiation is shown in Figure 3-3 [109]. The ultrasonic transducer continuously operated at 850 kHz under the atmosphere air. The electrical power output is 120 W. The maximum ultrasonic power was determined through calorimetric measurement to be 40 W, and the diameter of the ultrasonic transducer is 5 cm. Thus, the maximum acoustic intensity is  $2 \text{ W cm}^{-2}$ . The temperature of the bulk liquid inside the reactor was maintained at 295 K by 283 K circulating cooling water. Organic substrates were diluted to a given concentration with pure water (Millipore, Milli-Q Gradient A-10, R=18.2 M $\Omega$  cm). The irradiation volume was kept constant at 500 mL.

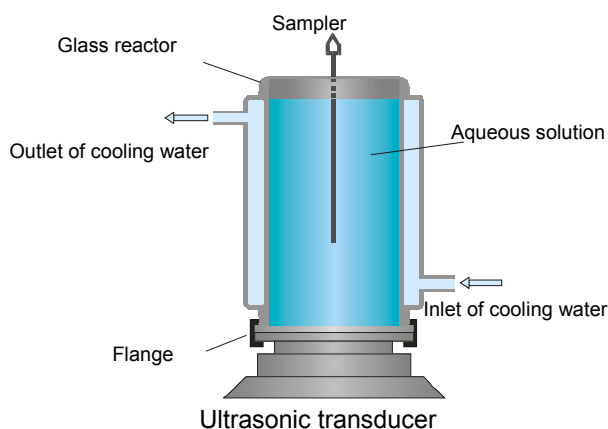


Figure 3-3 Scheme of the applied apparatus for ultrasonic irradiation  
Source: J. Lifka [109]

### 3.2.2 Ultrasound Setup for Nonaqueous Solutions

The device consists of an ultrasonic processor (UP200S or UP50H, Figure 3-4) with a titanium probe (Dr. Hielscher GmbH, Stuttgart) and a cylindrical glass reactor. The technological parameters of the ultrasonic device are detailed on the website of Dr. Hielscher GmbH [158].



Figure 3-4 Ultrasonic processor with a titanium probe  
Source: Dr. Hielscher GmbH [158]



The scheme of the applied apparatus for ultrasonic irradiation is shown in Figure 3-5 [10]. The ultrasonic processor UP200S continuously worked at 24 kHz under the atmosphere of dry-air. The acoustic intensity was estimated through caloric measurements and regulated between 15 and 60 W cm<sup>-2</sup>. The ultrasonic processor UP50H continuously worked at 30 kHz under the atmosphere of dry-air. The acoustic intensity was estimated through caloric measurement and regulated between 138 and 251 W cm<sup>-2</sup>.

The temperature of the bulk liquid is maintained at normal temperature (283 or 288 K) by circulating cooling water, and low temperature (208 K) by the mixture of dry-ice and isopropanol. The range of the irradiation volume was 2.5 - 20 mL.

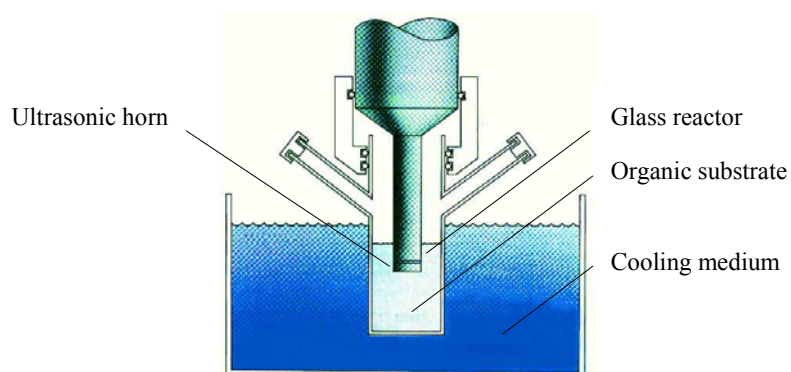


Figure 3-5 Scheme of an ultrasonic horn setup  
Source: K. S. Suslick [10]

### 3.3 Ultrasonic Power Measurement

The acoustic power entering the system was determined by calorimetry. The temperature ( $T$ ) of the reaction mixture was recorded, using a thermocouple, against time ( $t$ ), at 5 min intervals from the commencement of sonication. The acoustic powers were calculated using the following equation [118, 159, 160]:

$$P_{us} = \frac{dT}{dt} C_p M \quad (E\ 3-1)$$

where  $dT/dt$  is the temperature rise,  $C_p$  is the heat capacity of water (4186 J kg<sup>-1</sup>K<sup>-1</sup>) and  $M$  is the mass of water used (kg).

### 3.4 Analysis

VVOCs (Very Volatile Organic Compounds, b.p. < 100 °C) in aqueous solutions were quantitatively analyzed by headspace/GC/FID, and qualitatively by headspace/GC/MS. VOCs (Volatile Organic Compounds, b.p.: 100 ~ 260 °C) in aqueous solutions were qualitatively analyzed by SPME (solid phase micro extraction)/GC/MS. Organic compounds in organic liquids were quantitatively analyzed by autosampler/GC/FID, and qualitatively analyzed by autosampler/GC/MS. The following instruments were applied:

#### 3.4.1 Sampler

For each sampling time, two parallel samples were taken and analyzed. The averages of two parallel data of samples were calculated and taken into account in analyses of the sonochemical kinetics.

(1) DANI Headspace Sampler HSS 86.50 (see Figure 3-6)

Headspace conditions: Equilibration time was 20 min at 70 °C. The carrier gas was nitrogen (99.999%). Injection volume was 100 µL vapor.

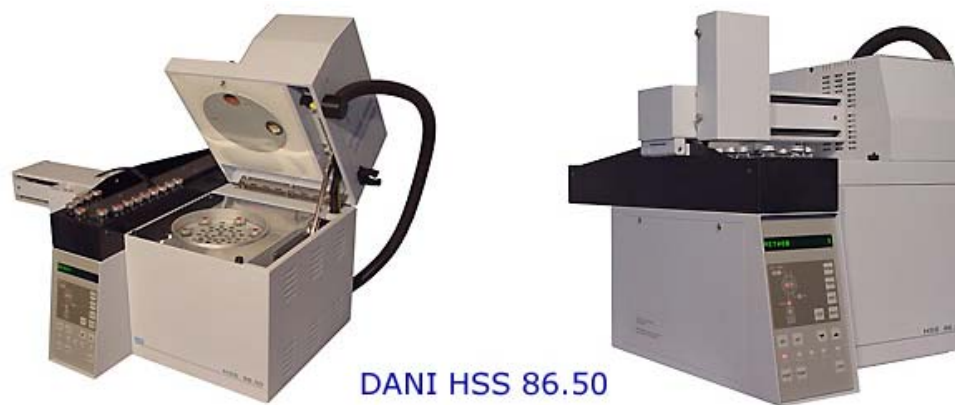


Figure 3-6 Headspace sampler DANI HSS 86.50

Source: DANI Instruments [161]

(2) SPME

Solid Phase Microextraction (SPME) is an innovative, solvent-free technology that is fast, economical, and versatile. The samplers were provided by SUPELCO. SPME is a fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both. The fiber coating removes the compounds from the sample by absorption in the case of liquid coatings or adsorption in the case of

solid coatings. The SPME fiber is then inserted directly into the gas chromatograph for desorption and analysis (Figure 3-7).

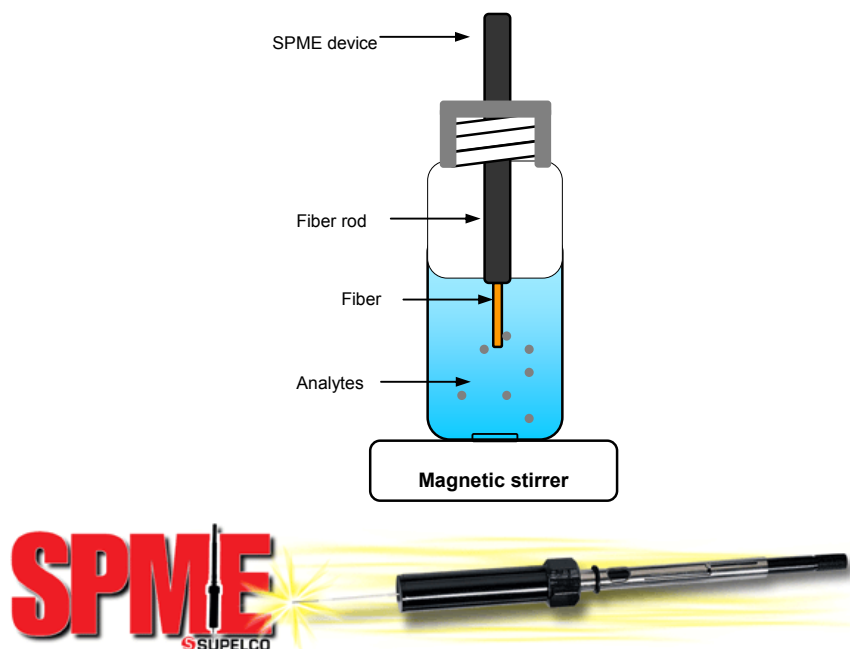


Figure 3-7 Schematic Diagram of SPME Process  
Source: SUPELCO [162]

The following SPME fibers were applied:

- (a) Red SPME Fiber Assemblies with 100  $\mu\text{m}$  polydimethylsiloxane (57300U);
- (b) Orange SPME Fiber Assemblies with 65  $\mu\text{m}$  carbowax/divinylbenzene (57312);
- (c) Gray SPME Fiber Assemblies with 50/30  $\mu\text{m}$  divinylbenzene/carboxen (57348U).

SPME fibers were respectively immersed 20 ~ 60 min in 10 or 20 mL aqueous solutions with agitations depending on the concentration of analyte. After sampling, the SPME fiber was inserted directly into the injector of GC for desorption and analysis.

### 3.4.2 Gas Chromatography

The quantitative analyses of organic compounds were calibrated by the standard solutions of the selected hydrocarbons such as benzene ( $R^2 = 0.999$ ), cyclohexene ( $R^2 = 0.993$ ), and 1,3-cyclohexadiene ( $R^2 = 0.995$ ). GC response factors of the various compounds were determined and shown in corresponding sections when the concentrations needed to be calculated.

(1) GC/FID for VVOCs analysis:

HP5890 series II with autosampler and FID, HP-5 capillary column: 30 m × 0.32 mm × 0.25 μm. The carrier gas is H<sub>2</sub> ( $P_i = 3$  or 10 psi depending on the nature of analyte). GC oven temperature was held at 35 °C for 5 ~ 7 min.

(2) GC/MS for VVOCs and VOCs analysis:

(a) HP 5890 series II with HP 5972 series mass selective detector, HP-5MS capillary column: 30 m × 0.25 mm × 0.25 μm. The carrier gas is He ( $P_i = 5$  psi). For the analysis of VVOCs, GC oven temperature was held at 35 °C for 5 min, and then ramped up to 85 °C with 10 K min<sup>-1</sup>. For the analysis of VOCs, GC oven temperature was held during the first 5 min at 35 °C, and then ramped up to 200 °C with 10 K min<sup>-1</sup>, kept constant for 10.5 min.

(b) Agilent Technologies GC 6890N / MSD 5973 Network with autosampler and MSD Chemstation D: 01.00. HP-5MS capillary column: 30 m × 0.25 mm × 0.25 μm. The carrier gas is He ( $P_i = 8$  psi). For the analysis of VVOCs, GC oven temperature was held at 35 °C for 5 min, and then ramped up to 85 °C with 10 K min<sup>-1</sup>. For VOCs analysis, GC oven temperature was held during the first 5 min at 35 °C, then ramped up to 250 °C with 10 K min<sup>-1</sup>, kept constant for 3.5 min.

(c) It should be noted that the extremely volatile species (< C<sub>4</sub>) cannot be analyzed by HP-5 and HP-5MS. In some cases, the Chromatogram Plot Supelcowax capillary column (Plot column: 30 m × 0.25 mm × 0.25 μm) was used to analyze the smaller species (< C<sub>4</sub>).

### 3.4.3 UV/Vis Analysis of DPPH

A 60.0 mmol L<sup>-1</sup> DPPH (2,2-diphenyl-1-picrylhydrazyl) solution was prepared by dissolving 139.0 mg DPPH (85%) in 5.0 mL methanol. 20 or 50 μL of 60.0 mmol L<sup>-1</sup> DPPH solutions were added to 3.0 mL of organic substrate to detect the rate of DPPH consumption respectively.

Absorption spectra of DPPH in the organic substrates were recorded with a Shimadzu UV-2102PC spectrophotometer ( $\lambda_{\text{max}} = 517$  nm). The corresponding pure organic substrates were used as blank solutions respectively.

## 4 Results of Sonolyses of Volatile Organic Substrates in Aqueous Solutions

### 4.1 Aquasonolyses of Selected C<sub>6</sub>H<sub>X</sub> Hydrocarbons

#### 4.1.1 Aquasonolytic Rate Constants of Selected Cyclic Hydrocarbons

Aquasonolytic curves and the integrated rate equations of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, cyclohexane, and methylcyclopentane were observed as shown in Figure 4-1 and Table 4-1. The correlation coefficient R<sup>2</sup> values show that sonolyses of the selected compounds in aqueous solutions follows pseudo-first-order kinetics. The aquasonolytic rate constants ( $k_{obs}$ , min<sup>-1</sup>) of various cyclic C<sub>6</sub>H<sub>X</sub> show a nearly 6-fold variation at identical conditions of ultrasonic irradiation. The aquasonolytic rate constants of the selected compounds have the following order: methylcyclopentane (0.1273) > cyclohexane (0.1036) > cyclohexene (0.0649) > 1,3-cyclohexadiene (0.0596) > 1,4-cyclohexadiene (0.0467) > benzene (0.0221). The reasons of the difference will be discussed in Section 6.1.

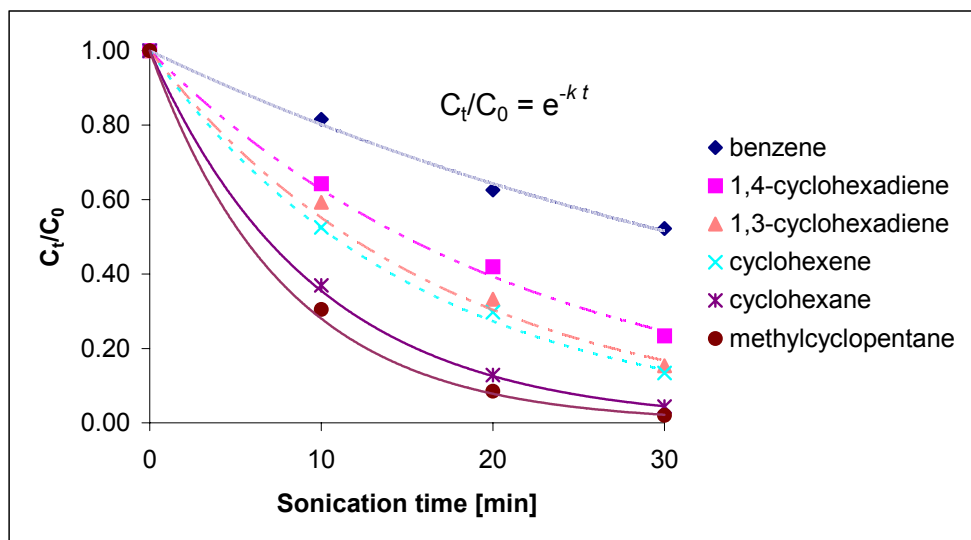


Figure 4-1 Aquasonolytic curves of cyclic C<sub>6</sub>H<sub>X</sub> hydrocarbons

(0.5 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Table 4-1 Integrated rate equations of aquasonolyses of selected  $C_6H_X$  hydrocarbons  
(0.5 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Cyclic $C_6H_X$ hydrocarbons	Aquasonolytic equations	R <sup>2</sup>	Aliphatic $C_6H_X$ hydrocarbons	Aquasonolytic equations	R <sup>2</sup>
benzene	$\frac{C_t}{C_0} = e^{-0.0221 t}$	0.9952	2-hexyne	$\frac{C_t}{C_0} = e^{-0.0385 t}$	0.9812
1,4-cyclohexadiene	$\frac{C_t}{C_0} = e^{-0.0467 t}$	0.9933	3-hexyne	$\frac{C_t}{C_0} = e^{-0.0412 t}$	0.984
1,3-cyclohexadiene	$\frac{C_t}{C_0} = e^{-0.0596 t}$	0.9894	1-hexyne	$\frac{C_t}{C_0} = e^{-0.0598 t}$	0.9913
cyclohexene	$\frac{C_t}{C_0} = e^{-0.0649 t}$	0.9951	2,3-dimethyl-2-butene	$\frac{C_t}{C_0} = e^{-0.1026 t}$	0.995
cyclohexane	$\frac{C_t}{C_0} = e^{-0.1036 t}$	0.9995	1,5-hexadiene	$\frac{C_t}{C_0} = e^{-0.1151 t}$	0.9961
methylcyclopentane	$\frac{C_t}{C_0} = e^{-0.1273 t}$	0.9975	2,3-dimethyl-1-butene	$\frac{C_t}{C_0} = e^{-0.1298 t}$	0.9966

#### 4.1.2 Aquasonolytic Rate Constants of Selected Aliphatic Hydrocarbons

Aquasonolytic curves and the integrated rate equations of 1-hexyne, 2-hexyne, 3-hexyne, 1,5-hexadiene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene were observed as shown in Figure 4-2 and Table 4-1. The correlation coefficient R<sup>2</sup> values show that sonolyses of the selected compounds in aqueous solutions follows pseudo-first-order kinetics. The aquasonolytic rate constants of various aliphatic  $C_6H_X$  show about a 3-fold variation at identical conditions of ultrasonic irradiation. The aquasonolytic rate constants of the selected compounds have the following order: 2,3-dimethyl-1-butene (0.1298) > 1,5-hexadiene (0.1151) > 2,3-dimethyl-2-butene (0.1026) > 1-hexyne (0.0598) > 3-hexyne (0.0412) > 2-hexyne (0.0385). The reasons of the difference will be discussed in Section 6.1.

#### 4.1.3 Products of Aquasonolyses of Selected $C_6H_X$ Hydrocarbons

The intermediates and products were qualitatively identified by GC/MS and/or GC/FID with retention time of standard samples after the sonication of 2.0 mmol L<sup>-1</sup> solutions treated at 850 kHz (40 W) ultrasound at 295 K.

##### 4.1.3.1 Very Volatile Products (VVPs)

Very volatile products (b.p. < 100 °C) may be generated directly through pyrolysis in cavitation bubbles. It has often been shown that hydrogen, methane, ethane, ethylene, and acetylene are major

products of sonolyses of hydrocarbons in aqueous solutions [6, 58, 63, 163]. Figure 4-3 shows products distribution of aquasonalyses of hexynes. Obviously, the ultrasonic cleavage of hexynes occurs in water. The C<sub>1</sub>-C<sub>5</sub> species were detected by plot GC-column during aquasonalyses of hexynes.

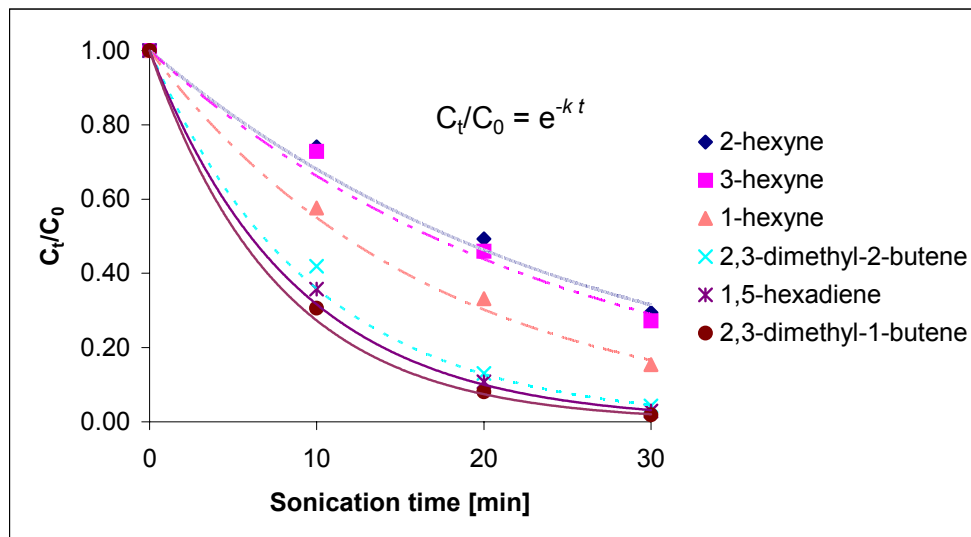


Figure 4-2 Aquasonalytic curves of aliphatic C<sub>6</sub>H<sub>X</sub> hydrocarbons  
(0.5 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

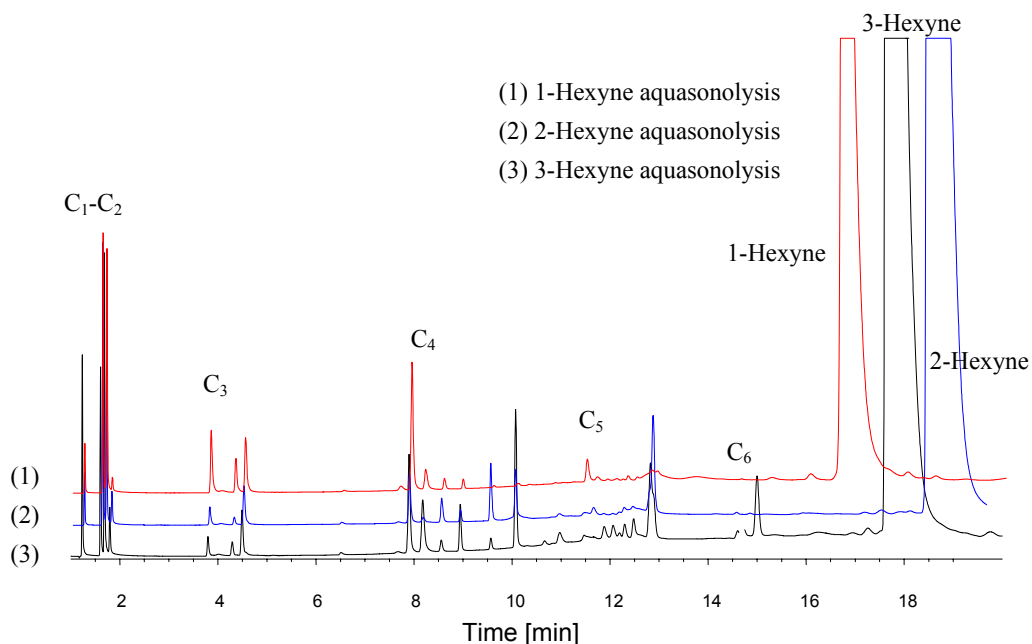


Figure 4-3 GC diagrams comparison of products from aquasonalyses of hexynes  
(2.0 mmol L<sup>-1</sup>, 850 kHz, 40 W, 295 K, 30 min.)

GC condition: Plot column (Cat.no.7551), Tc: 70 °C, 2 min, 10 °C min<sup>-1</sup>, 160 °C, 8min, P: 6 psi.

Since the small species cannot be detected by this sample method and HP-5MS GC-column, only the larger products ( $> C_4$  species) were considered by GC/MS.

Dehydrogenation and rearrangement occur during aquasonolyses of cyclohexene and cyclohexadiene. There, methylcyclopentadiene and benzene are the common products from aquasonolyses of the selected cyclic hydrocarbons. They are also generated by pyrolyses hydrocarbons [164]. Figure 4-4 shows a GC chromatogram of very volatile products from aquasonolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene.

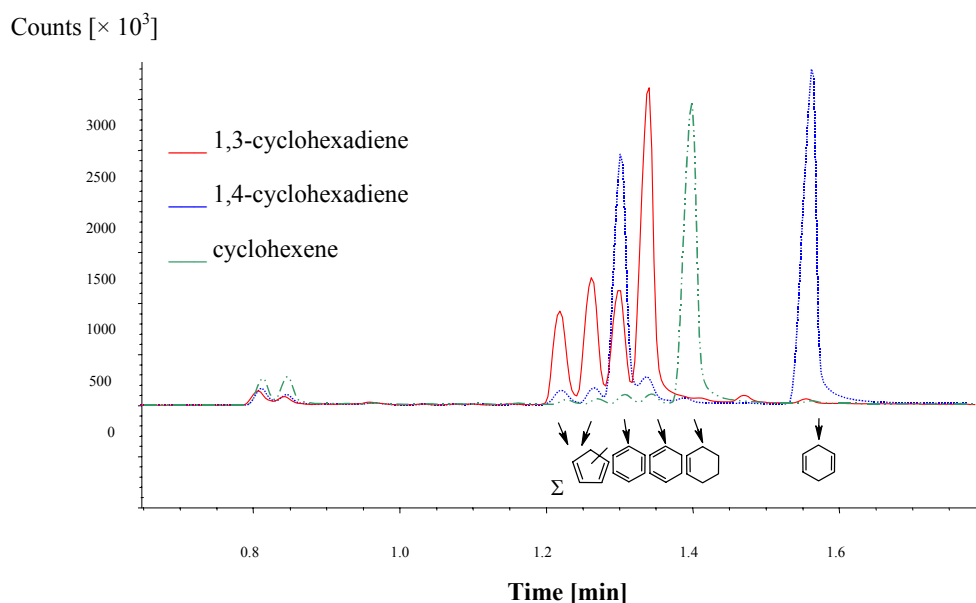
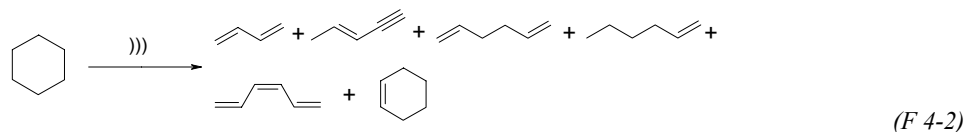
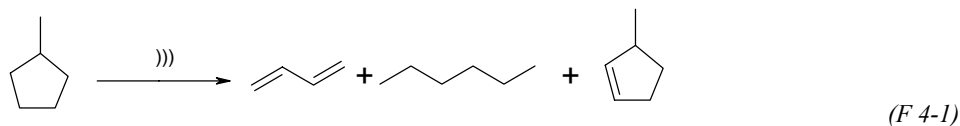


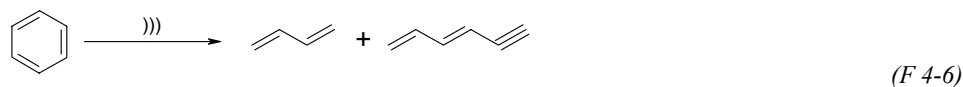
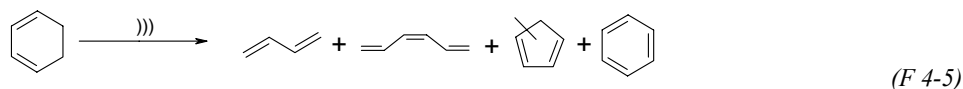
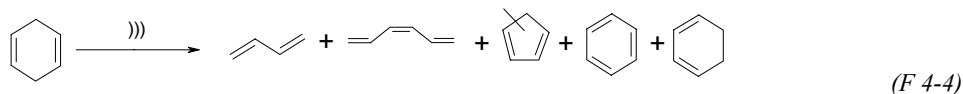
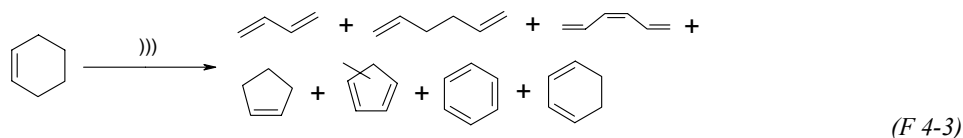
Figure 4-4 GC diagram of VVPs from aquasonolyses of selected  $C_6H_X$  hydrocarbons  
( $2.0 \text{ mmol L}^{-1}$ , 500 mL, 850 kHz, 40 W, 295 K, 60 min)

GC condition: HP-5MS column, Tc:  $35^\circ\text{C}$ , 2 min, P: 3 psi.

F4-1 to F4-6 show the major VVPs from the selected cyclic  $C_6H_X$  hydrocarbons.





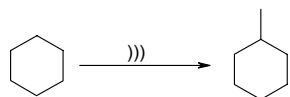


Except for smaller products (< C<sub>4</sub> species) from the pyrolysis in collapsing bubbles, benzene is major very volatile products from the aquasonolysis of 1,4-cyclohexadiene. The yields of methylcyclopentadiene and benzene from the 1,3-cyclohexadiene aquasonolysis are very close. However, the yields of C<sub>6</sub> species are very low from the aquasonolysis of cyclohexene. Smaller molecules (< C<sub>4</sub> species) were generated from aquasonolyses of methylcyclopentane, cyclohexane, and the selected aliphatic C<sub>6</sub>H<sub>X</sub>, here we did not detect the small products. Details of benzene formation during aquasonolyses of selected C<sub>6</sub>H<sub>X</sub> hydrocarbons will be discussed in Section 4.2 and 6.4.1.

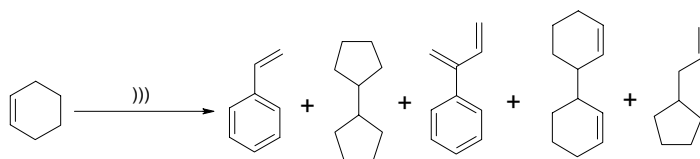
#### 4.1.3.2 Volatile Products (VPs)

The volatile and semi-volatile products (b.p.: 100 ~ 260 °C) can be generated by radical reactions at interfaces and in bulk liquids. No VPs from aquasonolyses of aliphatic C<sub>6</sub>H<sub>X</sub> and methylcyclopentane is detected, but many VPs could be detected from aquasonolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene. More VPs were found from the aquasonolysis of benzene, e.g. biphenyl and styrene, although their yields are very low, compared to the VVPs based on the GC diagrams. F4-7 to F4-11 show the major VPs from aquasonolyses of the selected cyclic hydrocarbons. There, styrene and 2-phenyl-1,3-butadiene are the common VPs of aquasonolyses of the selected hydrocarbons. Most of them are phenyl-compounds. Furthermore, biphenyl and phenyl-cyclohexadiene are generated relatively often. It indicates that vinyl-, 1,3-

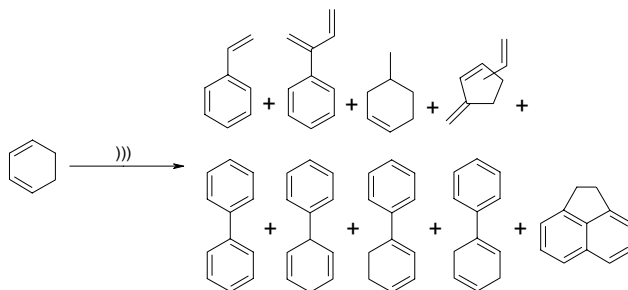
butadienyl-, and phenyl- are the common radicals generated in aquasonolyses of the selected hydrocarbons, thereof phenyl- is the most important radical.



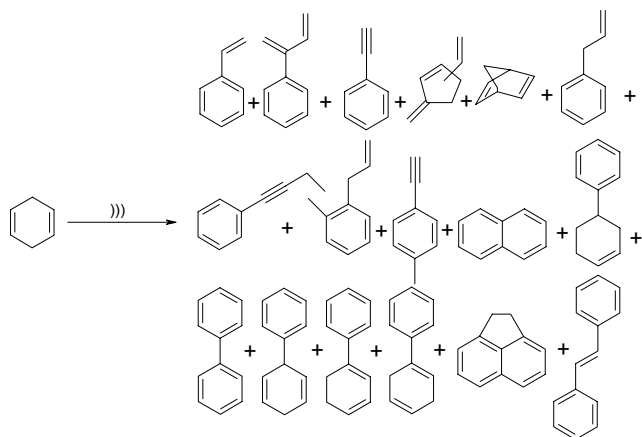
(F 4-7)



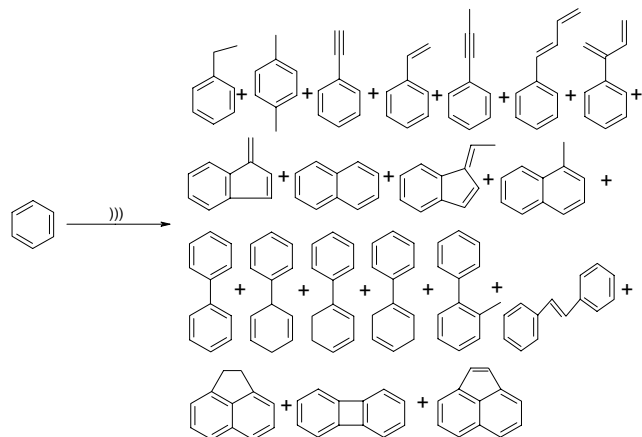
(F 4-8)



(F 4-9)



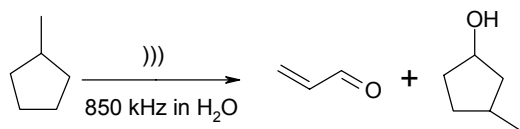
(F 4-10)



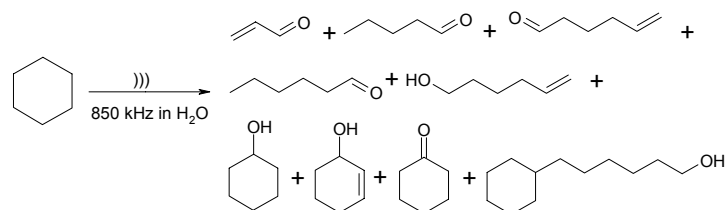
(F 4-11)

#### 4.1.3.3 Oxidation Products (OPs)

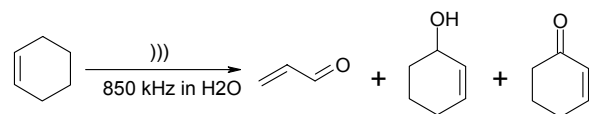
Hydroxyl radical and oxygen atom can be produced by sonolyses of water and oxygen in hot spots. Hydroxyl radicals may diffuse out of the bubble, or may eject out upon bubble collapse into the bulk phase. Hydroxyl radicals cause a series of radical reactions [79]. 2-Propenal is generated by reactions of oxygen atoms and propenyl-radicals in hot spots. Oxidation products from aquasonolyses of the selected hydrocarbons are shown in the following equations (F4-12 to F4-17):



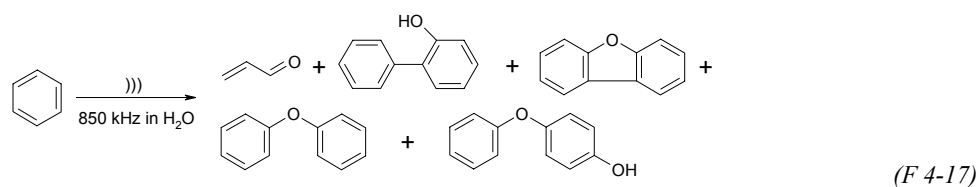
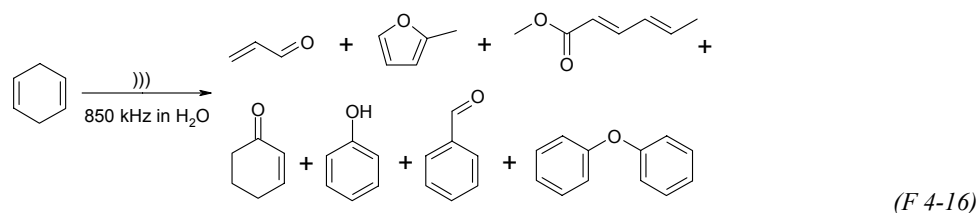
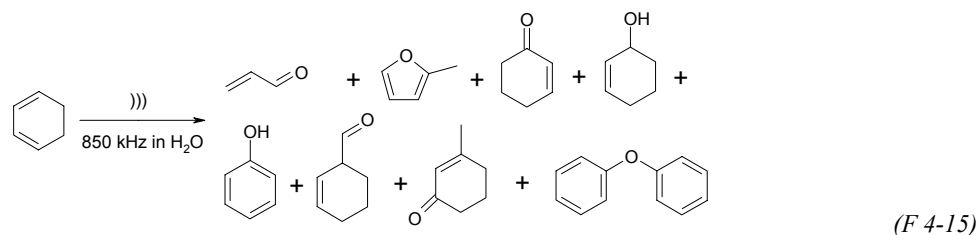
(F 4-12)



(F 4-13)



(F 4-14)



Most oxidation products were observed after sonication for 20 min. The selectivity is much less than the VVPs and VPs selectivity based on the GC diagrams. This shows that the oxidation process is not the major degradation pathway of the selected hydrocarbons under these experimental conditions.

Only a few oxidation products were generated during the aquasonolysis of methylcyclopentane. Therefore, most radicals produced during the sonolysis of methylcyclopentane quickly recombined into small molecules (< C<sub>4</sub> species) within bubbles, and few radicals are able to move into the interfacial region and bulk liquid.

Some aliphatic oxidation products are formed from the aquasonolysis of cyclohexane. With the increase of the water solubility of substrates, most oxidation products are nucleophilic substitution compounds on the ring, except for 2-propenal. 2-cyclohexen-1-ol, 2-cyclohexen-1-one. Diphenyl ether and other diphenyl-oxidation products are products of phenyl-radical reaction. However, no phenol is found during the aquasonolysis of benzene.

As a result, organic solutes with low water solubility easily transfer into cavitation bubbles and pyrolyzed in collapsing bubbles, thereby more small products were generated and aquasonolyses proceed rapidly. With an increase of water solubility, transport potential from the bulk liquid into cavitation bubbles decreases, so that more products from radical reactions at interfaces and in the bulk liquid are generated and aquasonolyses proceed more slowly.

## 4.2 Formation of Benzene during Aquasonolyses of the Selected C<sub>6</sub>H<sub>X</sub> Hydrocarbons

The kinetics of aquasonolyses of the selected C<sub>6</sub>H<sub>X</sub> hydrocarbons is reported in Section 4.1.3.1. The faster the aquasonolytic rate is, the more small products (< C<sub>4</sub> species) are formed. Benzene is generated by pyrolyses of the selected cyclic C<sub>6</sub>H<sub>X</sub> hydrocarbons [164]. If pyrolyses of hydrocarbons in hot spots is the predominant destruction pathway of their aquasonolyses, benzene should be observed during aquasonolyses. Therefore, the identification of benzene during aquasonolyses of hydrocarbons not only proves the mechanisms of sonolyses, but also confirms the reaction sites of aquasonolyses.

GC response factors of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene are determined as to be 1.00, 1.12, 1.12, and 1.09 respectively. Concentrations of the unknown C<sub>6</sub>H<sub>8</sub> were calculated based on GC response factor of cyclohexadiene.

### 4.2.1 Yield and Selectivity of Benzene during Aquasonolyses

Benzene is not found during aquasonolyses of methylcyclopentane and any of the aliphatic C<sub>6</sub>H<sub>X</sub>. The yield and selectivity of benzene produced during aquasonolyses of cyclohexene and cyclohexadiene are compared as shown in Figure 4-5 and Figure 4-6.

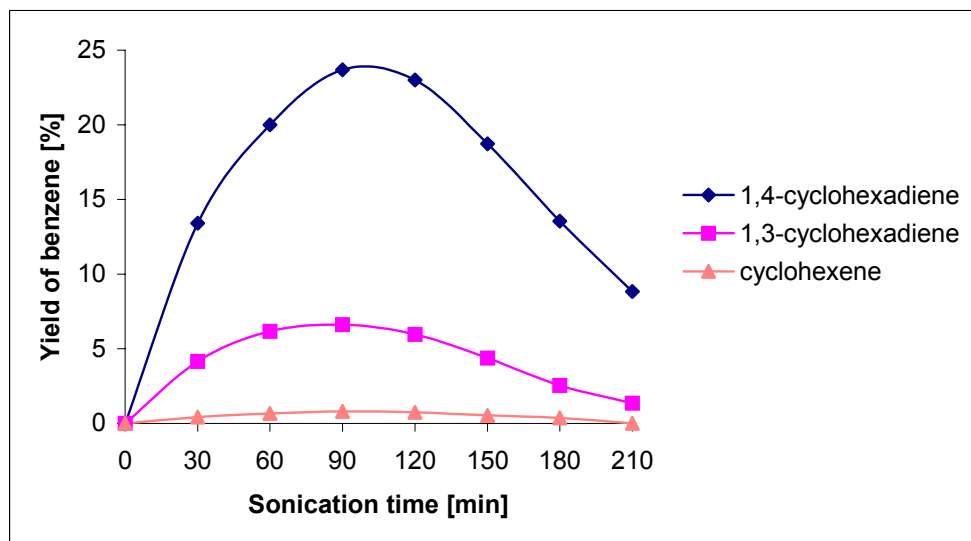


Figure 4-5 Yield of benzene produced during aquasonolyses of selected C<sub>6</sub>H<sub>X</sub> hydrocarbons (1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 27 W, 295 K)

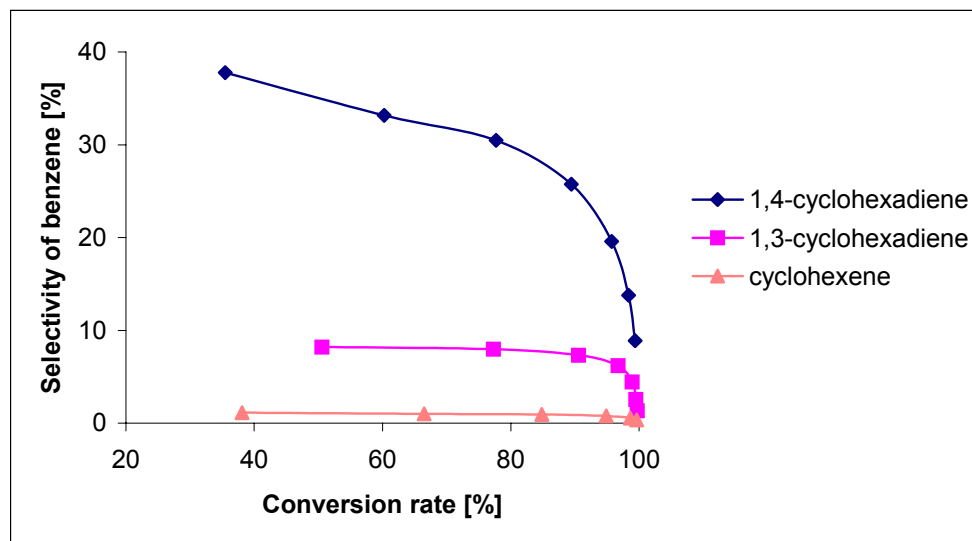


Figure 4-6 Selectivity of benzene produced during aquasonolyses of selected  $C_6H_x$  hydrocarbons (1.0 mmol  $L^{-1}$  solutions, 500 mL, 850 kHz, 27 W, 295 K)

The order of yield and selectivity of benzene produced are ranked as follows: 1,4-cyclohexadiene  $\gg$  1,3-cyclohexadiene  $\gg$  cyclohexene. In general, the small products ( $< C_4$  species) are the major species from sonolyses of volatile organic compounds in aqueous solutions, but the small products are not concerned and not identified in this work. In fact, it is important that benzene is the major  $C_6$  specie of products during the aquasonolysis of 1,4-cyclohexadiene. During aquasonolyses of 1,3-cyclohexadiene or cyclohexene,  $C_6H_8$  products and benzene are observed simultaneously.

In addition, benzene can be sonicated to yield smaller products and biphenyl during aquasonolyses of  $C_6H_x$  hydrocarbons (see *F4-6* and *F4-11*). At the start of sonication, the yield of benzene increases with sonication. Once the equilibrium between the generated and degraded products is reached, the yield of benzene decreases till benzene is completely sonicated. Moreover, the selectivity to benzene always decreases with sonication. While the conversion rate reaches 90%, the selectivity of benzene decreases sharply. These findings indicate that the generation rate of benzene is higher than its degradation rate.

In other words, the formal dehydrogenation of the selected  $C_6H_x$  hydrocarbons is a representative pathway of the generation for benzene. The order of sonolytic rates of the selected hydrocarbons is reported in Section 4.1.1.: methylcyclopentane  $>$  cyclohexane  $>$  cyclohexene  $>$  1,3-cyclohexadiene  $>$  1,4-cyclohexadiene  $>$  benzene. During the sonolysis of methylcyclopentane, no benzene or other  $C_6$  specie is found. Obviously, small organic fragments ( $< C_4$  species) are the major products from the sonolysis of methylcyclopentane. This indirectly indicates that small organic fragments may not be combined to yield benzene by ultrasonic irradiation in water.

### 4.2.2 Effect of the Initial Concentration on the Yield of Benzene

Since the ratio of specific heats of organic compounds is smaller than that of air (see Table 2-7), the collapse temperature may decrease when volatile organic compounds enter into cavitation bubbles. Figure 4-7 shows the effects of the initial concentration of C<sub>6</sub>H<sub>X</sub> hydrocarbons on the yields of benzene as a function of sonication time. Indeed, the yield of benzene is higher at low initial concentration than at high initial concentration at the beginning of sonication. With the sonication proceeding, the concentration of total volatile organic compounds decreases. Thus, the yield of benzene in the high concentration system exceeds that in the low concentration system. This also allows the conclusion that the degradation rate of benzene is slower in concentrated than in dilute solutions.

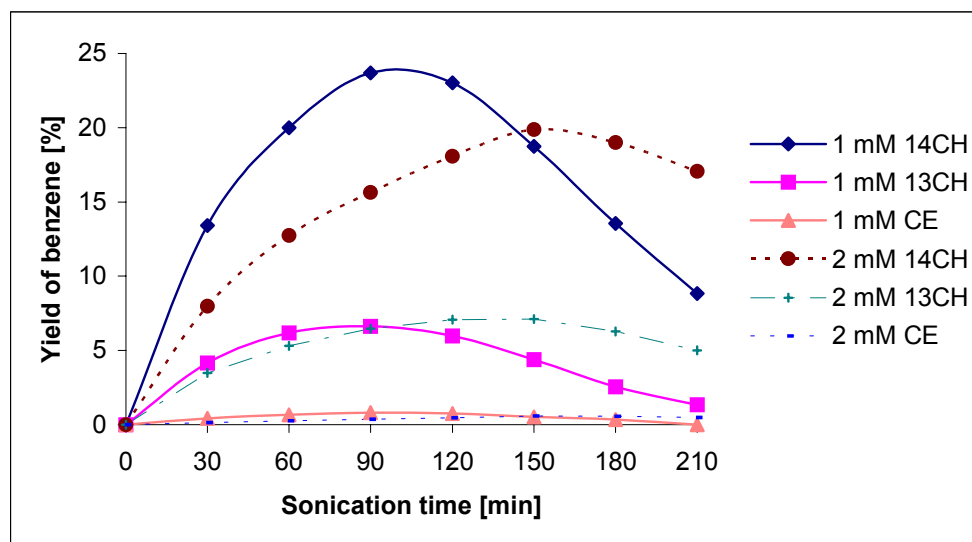


Figure 4-7 Effect of the initial concentration on yields of benzene during aquasonolyses (500 mL, 850 kHz, 27 W, 295 K; 14CH: 1,4-cyclohexadiene, 13CH: 1,3-cyclohexadiene, CE: cyclohexene)

### 4.2.3 Comparisons of Selectivity between Benzene and Other C<sub>6</sub> Products during the Aquasonolysis of 1,3-Cyclohexadiene

Except for benzene, other volatile products are also generated by aquasonolyses of C<sub>6</sub>H<sub>X</sub> hydrocarbons. Figure 4-8 shows the selectivity of C<sub>6</sub> products from the aquasonolysis of 1,3-cyclohexadiene.

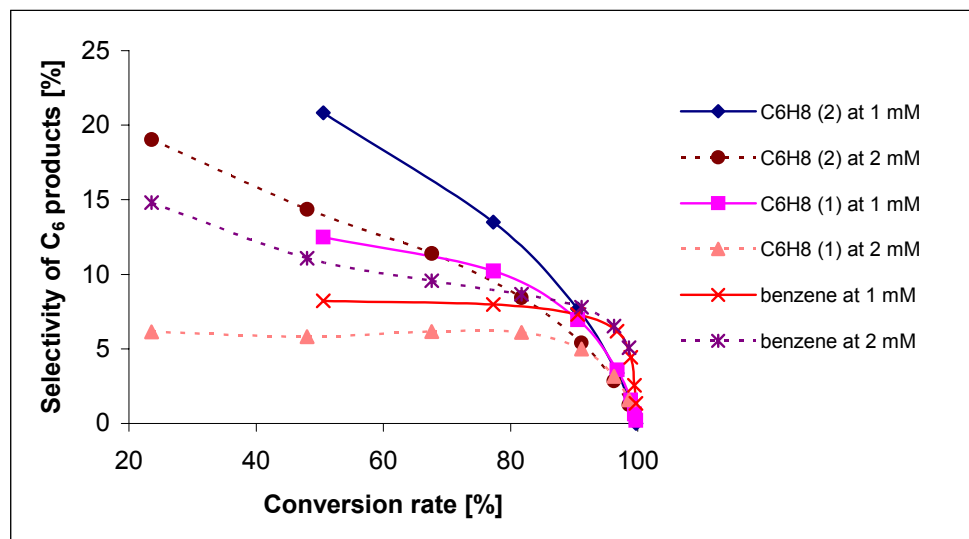


Figure 4-8 Selectivity of  $C_6$  products during the aquasonolysis of 1,3-cyclohexadiene (500 mL, 850 kHz, 27 W, 295 K)

$C_6H_8$  (1) and  $C_6H_8$  (2) are generated by C-C bond cleavage and molecular rearrangement of 1,3-cyclohexadiene. Both of  $C_6H_8$  were identified as methylcyclopentadienes by GC/MS. Based on conclusions of pyrolysis studies [164], methylcyclopentadienes are also the precursors of benzene in the pyrolysis. Indeed, benzene can be detected during the aquasonolysis of methylcyclopentadiene.

Methylcyclopentadiene and benzene can undergo further sonolyses. Figure 4-8 shows that the selectivity of methylcyclopentadienes at 1.0 mmol L<sup>-1</sup> solutions are higher than that of benzene till the conversion rate reaches 90%. Hence both the generation and the degradation rate of benzene are lower than those of methylcyclopentadienes. However, the selectivity of benzene obviously rises at 2.0 mmol L<sup>-1</sup> solution, since the higher concentration of organic compound causes the decrease of the collapse temperature of cavitation bubbles.

### 4.3 Aquasonolyses of Thiophene and Its Derivatives

Generally, the origin of sonochemistry is acoustic cavitation. The pyrolysis of volatile organic compounds in hot spots is the predominant aquasonolytic pathway of their decomposition [7]. Therefore, the identification of the mechanisms of the pyrolysis of thiophene would help us to understand the mechanisms of the sonolysis.

Since C-Cl bond cleavage was observed during ultrasonic irradiation of CCl<sub>4</sub> aqueous solution by Schmitt et al. in 1929 [5], only little is known about sonolyses of organic sulfur-containing



compounds. The first report on the sonolysis of thiophene was published in 1955 [20]. The authors reported the sonolysis of  $\alpha$ -iodothiophene at 600 kHz in a silver nitrate solution. Products after irradiation consisted of AgI, Ag<sub>2</sub>S, silver acetylide, and silver diacetylide. This study first documented the ultrasonic cleavage of the thiophene ring. Recently, very high intensity ultrasound was applied to treat a dilute solution of benzothiophene [31]. Some oxidation products were identified during ultrasonic irradiation. It is proposed that benzothiophene is oxidized by  $\cdot$ OH radicals.

In 1959 Wynberg and Bantjes [165] published a study on the pyrolysis of thiophene, in which a mixture of the three isomeric bithiophenes at 7-8 % conversion at 1123 K was obtained. Also, carbon disulfide, carbon, hydrogen sulfide, and traces of naphthalene, phenylthiophenes, and benzothiophene were detected in the pyrolyzate. In 2002, Winkler et al. [166] demonstrated the formation of carbon disulfide, hydrogen sulfide, and sulfur-containing polycyclic compounds such as dithiophene, benzothiophene, and phenylthiophene. In addition, the formation of carbon disulfide started at 1023 K and the yield increased to 57 % at 1273 K. The amount of 2,3'-dithiophene and benzothiophene reached a maximum at 1073 and 1173 K, respectively. Moreover, traces of sulfur-free aromatic hydrocarbons such as benzene, naphthalene, phenanthrene, fluoranthene, and pyrene were found above 1073 K. Recently, Memon et al. [167] reported on the kinetics of the pyrolysis of thiophene in shock tubes at 1598-2022 K. Acetylene was considered to be the main hydrocarbon product at all temperatures. Ethanethiol was found to be the major sulfur product, together with hydrogen sulfide at lower temperatures. Carbon disulfide was formed at higher temperatures. Additional products are CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>3</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>2</sub>.

In this work, the aquasonolytic kinetics and products of thiophenes are investigated.

#### 4.3.1 Aquasonolytic Rate Constants of Thiophene and Its Derivatives

The results of aquasonolyses of tetrahydrothiophene, thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and 2-ethylthiophene in dependence of time are shown in Figure 4-9. The integrated rate equations are listed in Table 4-2.

The correlation coefficient R<sup>2</sup> values in Table 4-2 indicate that aquasonolyses of the selected thiophenes indeed follow pseudo-first-order kinetics. This is consistent with aquasonolyses of hydrocarbons (Section 4.1.1 and 4.1.2) and other organic solutes [79, 168]. Aquasonolytic rate constants of various thiophenes show over a 2-fold variation at identical conditions of ultrasonic irradiation. Aquasonolytic rate constants ( $k_{obs}$ , min<sup>-1</sup>) follow the order of: 2-ethylthiophene (0.0176) > 2,5-dimethylthiophene (0.0160) > 2-methylthiophene (0.0130) > thiophene (0.0107) > tetrahydrothiophene (0.0069). The reasons of the difference will be discussed in Section 6.1.

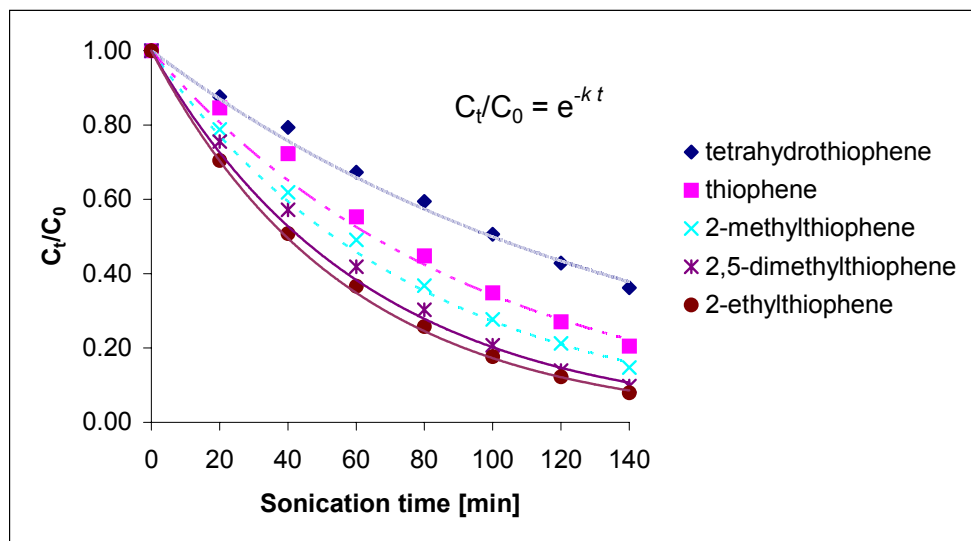


Figure 4-9 Aquasonolytic curves of thiophene and its derivatives  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Table 4-2 Integrated rate equations of aquasonolyses of thiophenes  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Substrates	Abbreviation	Aquasonolytic equations	R <sup>2</sup>
tetrahydrothiophene	TTH	$\frac{C_t}{C_0} = e^{-0.0069 t}$	0.9931
thiophene	TH	$\frac{C_t}{C_0} = e^{-0.0107 t}$	0.9879
2-methyl-thiophene	MTH	$\frac{C_t}{C_0} = e^{-0.0130 t}$	0.9943
2,5-dimethylthiophene	DMTH	$\frac{C_t}{C_0} = e^{-0.0160 t}$	0.9927
2-ethylthiophene	ETH	$\frac{C_t}{C_0} = e^{-0.0176 t}$	0.9977

### 4.3.2 Products from Aquasonolyses of Selected Thiophenes

#### 4.3.2.1 Very Volatile Products (VVPs)

It has been shown that hydrogen sulfide, acetylene, and other small species (< C<sub>4</sub>) are the major products during the aquasonolysis of iodothiophene and the pyrolysis of thiophene [20, 165-167].

Since the small species ( $< C_4$ ) cannot be detected by our analytic methods (sample and HP-5MS GC-column), the heavier species ( $> C_4$ ) were considered in this work. Figure 4-10 shows GC chromatograms of VVPs from aquasonolyses of the selected thiophenes. All samples were analyzed at 50% conversion rate of the substrates.

According to Figure 4-10,  $CS_2$ ,  $C_4H_4$ ,  $C_4H_2$ , and  $COS$  are the common very volatile products of aquasonolyses of the selected thiophenes. Most of them were previously observed in the pyrolysis of thiophene [20, 165-167].

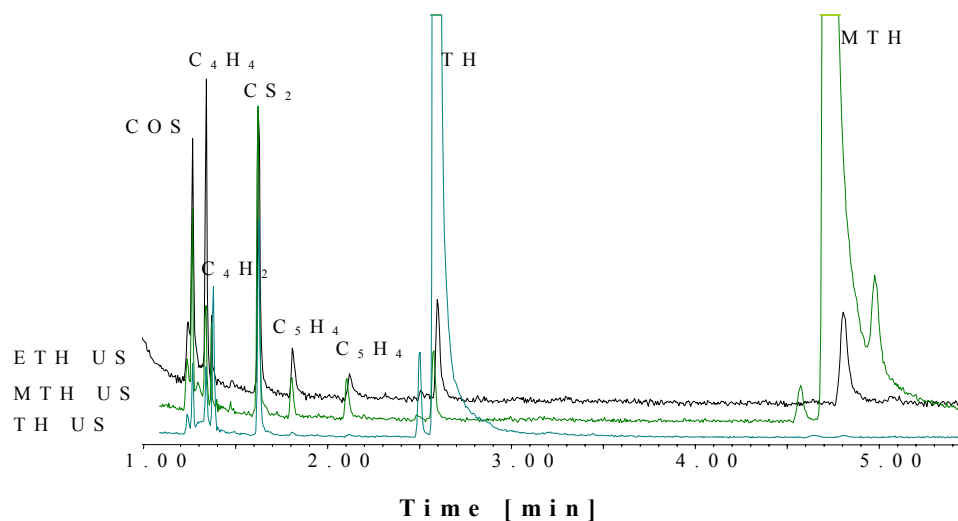


Figure 4-10 GC diagrams of VVPs from aquasonolyses of selected thiophenes  
( $1.0 \text{ mmol L}^{-1}$ ,  $500 \text{ mL}$ ,  $850 \text{ kHz}$ ,  $40 \text{ W}$ ,  $295 \text{ K}$ , at 50% conversion)

#### 4.3.2.2 Volatile Products (VPs)




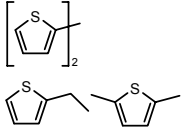

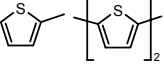

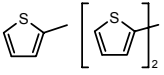
Some products, formed by cleavage of the C-C bond of an alkyl moiety, were detected. Thus, methylthiophene is a decomposition product of 2,5-dimethylthiophene and 2-ethylthiophene, and thiophene can be formed from 2-methylthiophene, 2,5-dimethylthiophene, and 2-ethylthiophene. Moreover, methylthiirane and several hydrocarbons with  $m/e$  78 including benzene were observed during aquasonolyses of 2,5-dimethylthiophene and 2-ethylthiophene.

In addition, VPs are products of the cleavage of bonds in thiophenes, as well as of the reaction of radicals formed during aquasonolyses.

Table 4-3 shows the VPs observed during aquasonolyses of thiophene and its derivatives. All samples were analyzed at 50% conversion of the substrates. Based on Table 4-3, dimers of thiophenes are the major common VPs occurring in aquasonolyses of thiophenes. Other VPs, e.g.

methylthiophene, are derived from the successive cleavage of higher substituted thiophenes. Moreover, fragments with  $m/e$  108 and 110 are frequently observed after aquasonolyses of various thiophenes. Their molecular formula could correspond to  $C_6H_4S$  and  $C_6H_6S$ . The detailed mechanism is the subject of our future studies. The formation of components with  $m/e$  124, 136 and 150 may be explained by similar reaction mechanisms. They may differ from the above-mentioned compounds by their degree of methyl- and ethyl substitution.

Table 4-3 Volatile products from aquasonolyses of thiophenes  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K, 50 % conversion)

Substrate	known VPs	unknown VPs (m/e)
TH (m/e: 84) 		108, 110
MTH (m/e: 98) 		108, 136
DMTH (m/e: 112) 		110, 112, 124, 126, 150
ETH (m/e: 112) 		108, 110, 136, 136, 208

Some oxidation products were identified during ultrasonic irradiation of a dilute solution of benzothiophene [31]. It is proposed that benzothiophene is oxidized by  $\cdot OH$  radicals. Unexpectedly, no OH-containing product is observed in this investigation. There are two reasons for failing to detect the OH-containing products. Firstly, the methods (SPME sample and/or GC/MS analysis) used are probably not suitable to detect products with OH group. Secondly, the amount of products with OH group generated is too low for the detection by GC analysis.

$\cdot OH$  radicals may oxidize benzothiophene more easily than thiophene, because the atmospheric OH rate constant of benzothiophene ( $3.0 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) is much higher than that of thiophene ( $0.95 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) [154]. In addition, the volatility and Henry's Law Constants of thiophenes ( $K_H = 61.9 \sim 434.7 \text{ kPa L mol}^{-1}$ ) are much higher than that of benzothiophene ( $K_H = 29.0 \text{ kPa L mol}^{-1}$ ), thus more volatile thiophenes can enter into the cavitation bubbles than benzothiophene. Future studies will investigate whether the OH-radicals or hydrogen peroxide react with thiophenes in water.

## 4.4 Aquasonolyses of Thioethers

In 1970, Spurlock et al. [26] reported the ultrasonic irradiation of 6.0 mmol L<sup>-1</sup> dibutyl sulfide in water. The major products of the irradiation of the aqueous suspension of dibutyl sulfide are dibutyl sulfoxide and butyl sulfonic acid. Minor products observed included dibutyl sulfone, butyric acid, carbon monoxide, ethylene, acetylene, and methane. In general, the origin of sonochemistry is acoustic cavitation. Pyrolyses of volatile organic compounds in hot spots may be the predominant aquasonolytic pathway [7]. Hydrophilic compounds in the bulk liquid could additionally react with free radicals ( $\cdot\text{OH}$ ,  $\cdot\text{H}$ ) produced by the sonolysis of water [7, 29, 79, 87, 146, 169, 170]. Therefore comprehending the mechanisms of pyrolyses of thioethers would help us understanding the mechanisms of sonolyses.

In 1955 Braye et al. published a study on the thermal decomposition of sulfides [171]. The pyrolysis of methyl benzyl sulfide ( $\text{CH}_3\text{SCH}_2\text{Ph}$ ) at 742 – 917 K gave  $\text{CH}_3\text{SH}$  and dibenzyl primarily. Additionally, small amounts of stilbene,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , and  $\text{H}_2$  are also formed. The pyrolysis of dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ ) at 931 and 982 K gave  $\text{CH}_4$ ,  $\text{CH}_3\text{SH}$ , and  $\text{H}_2\text{S}$ . The pyrolysis of dimethyl disulfide ( $\text{CH}_3\text{SSCH}_3$ ) at 735 – 833 K gave  $\text{CH}_3\text{SH}$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CH}_2=\text{CH}_2$ ,  $\text{CH}_3\text{CH}_3$ , and heavier sulfur compounds. Up to 1983, Davis et al. demonstrated the formation of 1,2-diphenylethane ( $\text{PhCH}_2\text{CH}_2\text{Ph}$ ) and diphenyl disulfide ( $\text{PhSSPh}$ ) during the pyrolysis of phenyl benzyl sulfide ( $\text{PhSCH}_2\text{Ph}$ ) at 1073 and 1173 K [172]. However, diphenyl sulfide ( $\text{PhSPh}$ ) was unreactive at Flash Vacuum Pyrolysis (FVP) temperatures of 1173 K. Gholami et al. [173] recently reported the gas-phase kinetics and mechanism of diallyl sulfide thermal decomposition at 433–463 K and 80 Torr. Propene and thiacrolein ( $\text{CH}_2=\text{CHCH}=\text{S}$ ) were regarded as the main product.

In this work, the aquasonolytic kinetics and products of thioethers are noted.

### 4.4.1 Aquasonolytic Rate Constants of Thioethers

The results of aquasonolyses of the selected thioethers in dependence of time are shown in Figure 4-11. The integrated rate equations are listed in Table 4-4.

The correlation coefficient  $R^2$  values in Table 4-4 indicate that aquasonolyses of the selected compounds follow pseudo-first-order kinetics well. This is consistent with aquasonolyses of hydrocarbons (Section 4.1.1 and 4.1.2), thiophenes (Section 4.3.1), and other organic compounds [87, 168]. Aquasonolytic rate constants of various thioethers show the larger variation at identical conditions. Aquasonolytic rate constants ( $k_{obs}$ ,  $\text{min}^{-1}$ ) are ranked as follows: diethyl disulfide (0.0519) > dipropyl disulfide (0.0476) > diallyl sulfide (0.0431) > dibutyl sulfide (0.0407) > dipropyl sulfide (0.0381) > diethyl sulfide (0.0371). The reasons will be discussed in Section 6.1.

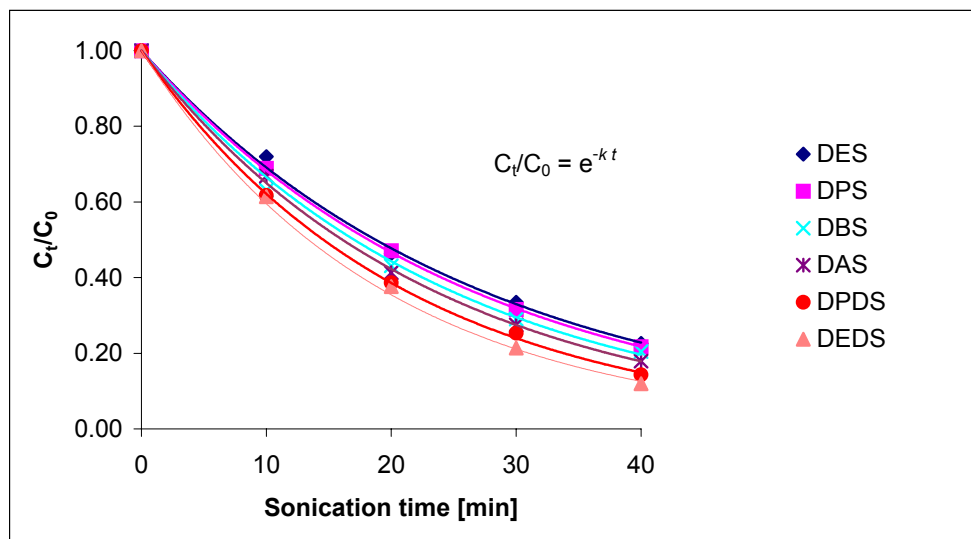


Figure 4-11 Aquasonolytic curves of thioethers  
(0.2 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Table 4-4 Integrated rate equations of aquasonolyses of thioethers

(0.2 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Substrates	Abbreviation	Aquasonolytic equations	R <sup>2</sup>
diethyl disulfide	DEDS	$\frac{C_t}{C_0} = e^{-0.0519 t}$	0.9974
dipropyl disulfide	DPDS	$\frac{C_t}{C_0} = e^{-0.0476 t}$	0.998
diallyl sulfide	DAS	$\frac{C_t}{C_0} = e^{-0.0431 t}$	0.9993
dibutyl sulfide	DBS	$\frac{C_t}{C_0} = e^{-0.0407 t}$	0.9965
dipropyl sulfide	DPS	$\frac{C_t}{C_0} = e^{-0.0381 t}$	0.9998
diethyl sulfide	DES	$\frac{C_t}{C_0} = e^{-0.0371 t}$	0.998

#### 4.4.2 Products from Aquasonolyses of the Selected Thioethers

##### 4.4.2.1 Very Volatile Products (VVPs)

It has been shown that CO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>4</sub> are formed during the sonolysis of dibutyl sulfide in water [26]. Figure 4-12 shows total ions chromatograms of GC/MS of VVPs from aquasonolyses of the selected thioethers. Carbon disulfide, thiols, thiophene, thiirane, and smaller sulfides (e.g.

methyl ethyl sulfide, ethyl propyl sulfide, or ethyl allyl sulfide) are the most common sulfur-containing products during aquasonolyses of the selected substrates.  $C_4H_4$  and  $C_4H_2$  are the most common hydrocarbon products. In addition, more hydrocarbons can be observed during aquasonolysis of diallyl sulfide, such as cyclopentadiene, 1,5-hexadiene,  $C_6H_8$ , and benzene. Furthermore, some oxidation products can be detected, such as COS and propanal from dipropyl sulfide, and propanal from diallyl sulfide. All these products demonstrate that thioethers undergo pyrolyses during their aquasonolyses.

#### 4.4.2.2 Volatile Products (VPs)

In general, VPs are products generated by oxidation, dissociation of substrates, as well as free radical reactions. Table 4-5 shows VPs from aquasonolyses of thioethers. According to this table, the sulfurized and cyclized products are the most common VPs from aquasonolyses of thioethers. Dipropyl sulfoxide from dipropyl sulfide was found as the oxidized product of sulfide. Other VPs, such as methyl ethyl disulfide, ethyl propyl disulfide, and ethyl butyl disulfide from diethyl disulfide, are formed by a network of free radical reactions.

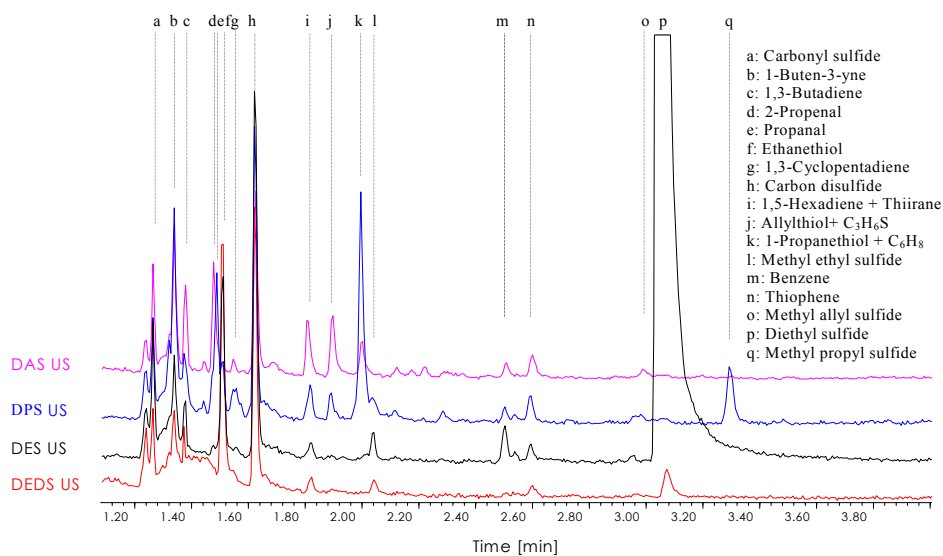


Figure 4-12 Total ions chromatograms of VVPs from aquasonolyses of selected thioethers (1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K, at 70 % conversion)

Table 4-5 Volatile products from aquasonolyses of thioethers

(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K, 70% conversion)

Substrates	Sulfurized products	Cyclized products	Others
DES 			-
DPS 			
DEDS 			
DAS 		dimethylthiophene	-

#### 4.5 Aquasonolyses of N-Heterocyclic Compounds

In 1956, Zechmeister et al. reported the ultrasonic cleavage of the pyridine ring in aqueous silver nitrate [21]. Roughly 5% of the ring atoms are precipitated as a mixture of silver acetylide, silver diacetylide and silver cyanide. It has been shown that similar cleavage reactions can also be realized in the absence of silver, with pyridine and pyrrole. Under these conditions, free acetylene and hydrogen cyanide evolved [22]. The effect of pH and dissolved gases on the ultrasonic reaction of aqueous solutions of pyridine to produce acetylene has been published in 1963 [32]. Pyridine in acidic solution is essentially unaffected by ultrasonic waves. The rate of the production of acetylene is dependent on the ratios of specific heats of the dissolved gases. The rate of the ultrasonic cleavage of the pyridine ring is shown to be independent on the surface tension of the reaction solution.

Thus, pyrolyses of N-heterocycles in the exploding cavitation bubbles can also occur. In this work, the aquasonolytic kinetics and products of pyrrole, N-methylpyrrole, and pyridine are investigated. Pyrrole and N-methylpyrrole were analyzed quantitatively by headspace/GC/FID. Pyridine was analyzed quantitatively by solvent extraction – GC / FID. 1.2 mL benzene was added into 10 mL sample to extract pyridine.



### 4.5.1 Aquasonolytic Rate Constants of the Selected N-Heterocycles

The concentration changes of aquasonolyses of the selected N-heterocycles in dependence of time are shown in Figure 4-13. The integrated rate equations are listed in Table 4-6.

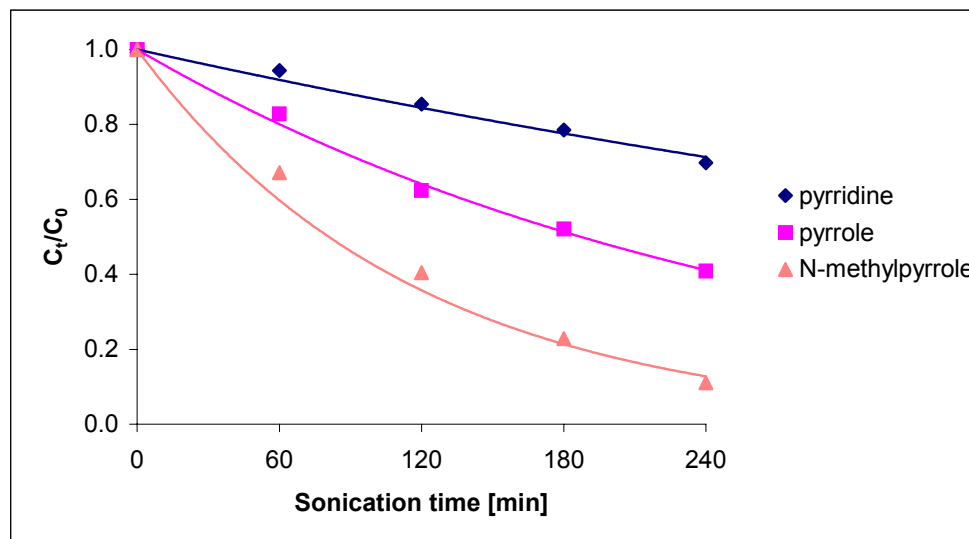


Figure 4-13 Aquasonolytic curves of pyrrole, N-methylpyrrole, and pyridine  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

The correlation coefficient  $R^2$  values in Table 4-6 indicate that aquasonolyses of the selected N-heterocycles follow pseudo-first-order kinetics. This is consistent with aquasonolyses of hydrocarbons, thiophenes, and thioethers (Section 4.1.1, 4.3.1, 4.4.1). Aquasonolytic rate constants of various N-heterocycles show around 6-fold variation at identical conditions of ultrasonic irradiation. Aquasonolytic rate constants ( $k_{obs}$ , min<sup>-1</sup>) are ranked as follows: N-methylpyrrole (0.0086) > pyrrole (0.0037) > pyridine (0.0014). The reasons of the difference will be discussed in Section 6.1.

Table 4-6 Integrated rate equations of aquasonolyses of the selected N-heterocycles

(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Substrates	Aquasonolytic equations	R <sup>2</sup>
N-methylpyrrole	$\frac{C_t}{C_0} = e^{-0.0086 t}$	0.983
Pyrrole	$\frac{C_t}{C_0} = e^{-0.0037 t}$	0.996
Pyridine	$\frac{C_t}{C_0} = e^{-0.0014 t}$	0.983

### 4.5.2 Products from Aquasonolyses of the Selected N-Heterocycles

Very volatile products are directly formed through pyrolysis of substrates during the collapse of the cavitation bubbles. It has been previously proven that acetylene, diacetylene and hydrogen cyanide can be formed during aquasonolyses of pyrrole, N-methylpyrrole, and pyridine [21, 22, 32].

Because of slow aquasonolytic rates of pyrrole and pyridine, sonolytic yields are very low. No product was found from the aquasonolysis of 5 mmol L<sup>-1</sup> pyridine in 6 h, although the colorless pyridine solution gradually became slight brown during the aquasonolysis. Only little HCC-CN and benzene were found from the aquasonolysis of 5 mmol L<sup>-1</sup> pyrrole in 6 h. The colorless pyrrole solution became yellow little by little. In contrast, the colorless N-methylpyrrole solution became yellow in 30 min of ultrasonic irradiation. Furthermore, more products from the aquasonolysis of N-methylpyrrole were identified by headspace and/or SPME /GC/MS. Figure 4-14 shows total ions chromatograms of GC/MS of VVPs from the aquasonolysis of N-methylpyrrole. There, HCC-CN and H<sub>2</sub>C=CHCN are the most common nitrogen-containing products. C<sub>4</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>X</sub> are the major hydrocarbon products. In addition, benzene and some products with m/e 64 can be observed. No oxidation product and larger molecular (> C<sub>6</sub> species) is found. However, these volatile products demonstrate that N-methylpyrrole undergoes the pyrolysis during the aquasonolysis.

It is interesting to further investigate the oxidized products from pyridine and pyrrole, since their water solubilities are relatively high. Oxidation may be an destruction pathway in this case.

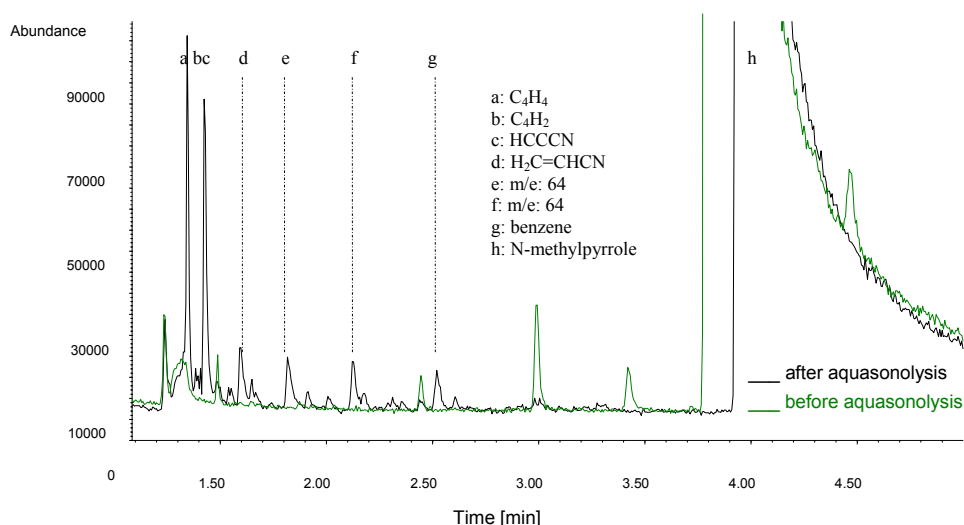


Figure 4-14 Total ions chromatograms of VVPs from the aquasonolysis of N-methylpyrrole (5.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K, 4 h Analysis: headspace, HP-5MS, GC/MS)

## **5 Results of Sonolyses of Volatile Organic Substrates in Nonaqueous Liquids**

### **5.1 Sonolyses of Aliphatic and Cyclic C<sub>6</sub>H<sub>X</sub> Hydrocarbons**

Ultrasound irradiation causes cavitation and enables bond transformations and/or homolysis in many organic liquids dependent on their respective volatilities. Although it is essential to understand the sonochemical behavior of organic liquids, only a few examples of homogenous nonaqueous sonication have been reported since the 1950s [7, 8, 170].

In Chapter 4, the sonolytic kinetics and products of the selected C<sub>6</sub>H<sub>X</sub> hydrocarbons in aqueous solutions are described. Products are generated through the thermal decomposition of C<sub>6</sub>H<sub>X</sub> hydrocarbons in hot spots and radical reactions in the aqueous solutions. In order to further clarify the sonochemical mechanisms of hydrocarbons, the sonolytic products and yields from the pure liquids of C<sub>6</sub>H<sub>X</sub> hydrocarbons at normal and low temperature are investigated.

#### **5.1.1 Sonolyses of the Selected C<sub>6</sub>H<sub>X</sub> Hydrocarbons at Normal Temperature**

It has been previously demonstrated that hydrocarbons most efficiently convert under sonolytic conditions in which their vapor pressures range from 0.1 to 0.5 Torr (13.33-66.65 Pa) [43]. However, vapor pressures of C<sub>6</sub>H<sub>X</sub> hydrocarbons under investigation are over 66.6 Torr (8.88 kPa) at 298 K. Thus, it is difficult to cause cavitation bubbles in C<sub>6</sub>H<sub>X</sub> hydrocarbons by ultrasound irradiation at normal temperature (278 ~ 303 K). In order to test this theory, the selected C<sub>6</sub>H<sub>X</sub> hydrocarbons were irradiated by ultrasound at 288 K respectively. Table 5-1 shows the experimental results. Although some organic liquids become slight yellow or yellow after 30 min of ultrasonic irradiation, no product is found by GC/MS. Even though the ultrasonic irradiation on the selected hydrocarbons lasted 2 - 6 h at 288 K under 24, 30, and 850 kHz, no product was found yet. Indeed, a suitable vapor pressure of organic liquid appears to be essential for the sonolysis.

#### **5.1.2 Sonolyses of the Selected Aliphatic C<sub>6</sub>H<sub>X</sub> Hydrocarbons at Low Temperature**

The decreasing vapor pressure of the solvent increases the intensity of cavitation collapse, the maximum temperature of the collapse and the rates of sonochemical reactions [41, 146]. Therefore,

sonolytic products of  $C_6H_X$  hydrocarbons could be observed at the suitable temperature. However, even though the ultrasonic irradiation in 1,5-hexadiene was performed for 6 h in a mixture of water-ice-salt (258 K), no product was found yet. Thus, it is necessary to conduct sonolyses of  $C_6H_X$  hydrocarbons at a much low temperature (208 K).

Table 5-1 Sonolytic results of the selected  $C_6H_X$  compounds at normal temperature

Conditions	Organic liquids	Ultrasonic power [W]	Diameter of sonotrode [mm]	Sample volume [mL]	Irradiation time [min]	Phenomena	Products
UP50H: 30 kHz, 138 W cm <sup>-2</sup> 288 K,	n-hexane	10	2	2.0	30	Colorless	No
	n-hexane	10	2	1.0	60	Colorless	No
	1,5-hexadiene	10	2	2	20	Colorless	No
	1,5-hexadiene	10	2	4	30	Colorless	No
	1,4-cyclohexadiene	10	2	1	30	Colorless to slight yellow	No
	1,3-cyclohexadiene	10	2	1	30	Colorless to yellow liquid	No
	1,3-cyclohexadiene	15	2	2	120	Colorless to yellow liquid	No
	cyclohexane	20	2	2	60	Colorless	No
	cyclohexane	20	4	2	60	Colorless	No
	cyclohexene	10	4	1	30	Colorless	No
UP200S: 24 kHz, 44 W cm <sup>-2</sup> 288 K	cyclohexene	10	2	2	60	Colorless	No
	1,5-hexadiene	10	2	1	60	Colorless	No
UP200S: 24 kHz, 44 W cm <sup>-2</sup> 258 K	1,5-hexadiene	10	2	2	360	Colorless	No
850 kHz, 2 W cm <sup>-2</sup> 300 mL 295 K water bath	1,5-hexadiene	40	50	10	240	Colorless	No
	1,3-cyclohexadiene	40	50	2	240	Smog in headspace	No
	1,3-cyclohexadiene	40	50	2	360	Colorless	No

The sonolytic products of 1-hexyne, 2-hexyne, 3-hexyne, 1,5-hexadiene, 2,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene in the cold media of dry-ice/isopropanol mixture (208 K) were investigated. Ultrasonic frequency and intensity are 24 kHz and 45 W cm<sup>-2</sup> respectively. The irradiation volume and time are 2.5 mL and 4 h respectively. The ultrasonic irradiations were carried out in the atmosphere of dry-air.

In order to evaluate the sonolytic capacity of the model compounds, the sonolytic pseudo-yields of the model compounds were investigated. The sonolytic pseudo-yield ( $Y_{pseudo}$ ) is calculated as follows:

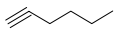


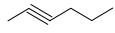


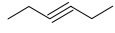
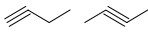

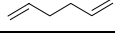




$$Y_{pseudo} = \frac{\sum A_{pi} - \sum A_{p0}}{A_s} \times 100\% \quad (E\ 5-1)$$

where  $\sum A_{pi}$  is the sum of GC peak areas of all products after the reaction,  $\sum A_{p0}$  is the sum of GC peak areas of compounds at corresponding spots at start of the reaction (blank values),  $A_s$  is the GC area of model substrate at start of the reaction.

Table 5-2 shows products identified by GC/MS analysis and pseudo-yields.

Table 5-2 Sonolytic products and pseudo-yields of selected aliphatic C<sub>6</sub>H<sub>X</sub> at low temperature

(24 kHz, 45 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h)

Substrates	Products				Phenomena	Pseudo-yield [%]
	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>		
1-hexyne 	C <sub>3</sub> H <sub>X</sub>				Colorless to slight yellow liquid	0.0218
2-hexyne 	C <sub>3</sub> H <sub>X</sub>	C <sub>4</sub> H <sub>4</sub> , 		C <sub>6</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>8</sub>	Colorless to slight yellow liquid	0.0273
3-hexyne 	C <sub>3</sub> H <sub>X</sub>			C <sub>6</sub> H <sub>12</sub>	Colorless to yellow liquid	0.0074
1,5-hexadiene 	C <sub>3</sub> H <sub>X</sub>	 , C <sub>4</sub> H <sub>X</sub>	C <sub>5</sub> H <sub>X</sub>	C <sub>6</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>8</sub>	colorless	0.0066
2,3-dimethyl-1-butene 		C <sub>4</sub> H <sub>8</sub> , C <sub>4</sub> H <sub>X</sub>		C <sub>6</sub> H <sub>10</sub>	colorless	0.0027
2,3-dimethyl-2-butene 		C <sub>4</sub> H <sub>4</sub> , C <sub>4</sub> H <sub>X</sub>	 C <sub>5</sub> H <sub>8</sub> ,	C <sub>6</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>10</sub>	colorless	0.0096

Clearly, some small molecules are formed during sonolyses of the selected aliphatic C<sub>6</sub>H<sub>X</sub> hydrocarbons at low temperature. The C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub> species generated from the cleavage of C-C bonds are most common. Furthermore, C<sub>6</sub>H<sub>X</sub> products from radical recombination can also be observed. However, larger species (> C<sub>6</sub>) are not found. C<sub>1</sub> and C<sub>2</sub> species are not detected in this work. Figure 5-1 to Figure 5-6 illustrate the changes observed by GC, before and after sonolyses of the selected aliphatic C<sub>6</sub>H<sub>X</sub> hydrocarbons.

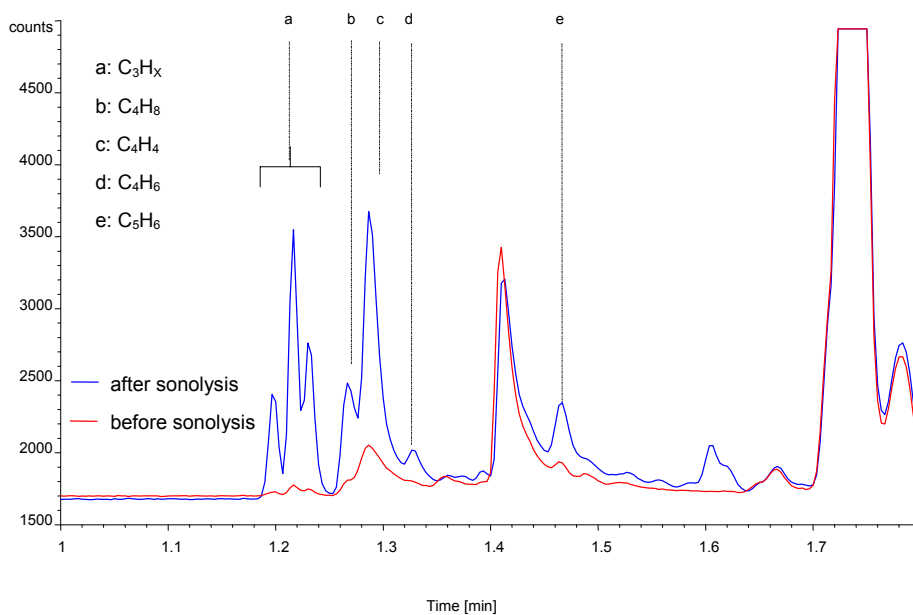


Figure 5-1 Gas chromatograms of products from the sonolysis of 1-hexyne

(GC conditions: column: HP-5; carried gas: H<sub>2</sub> (split injection); P: 3 Psi; T<sub>c</sub>: 35 °C; T<sub>i</sub>: 250 °C; T<sub>d</sub>: 290 °C)

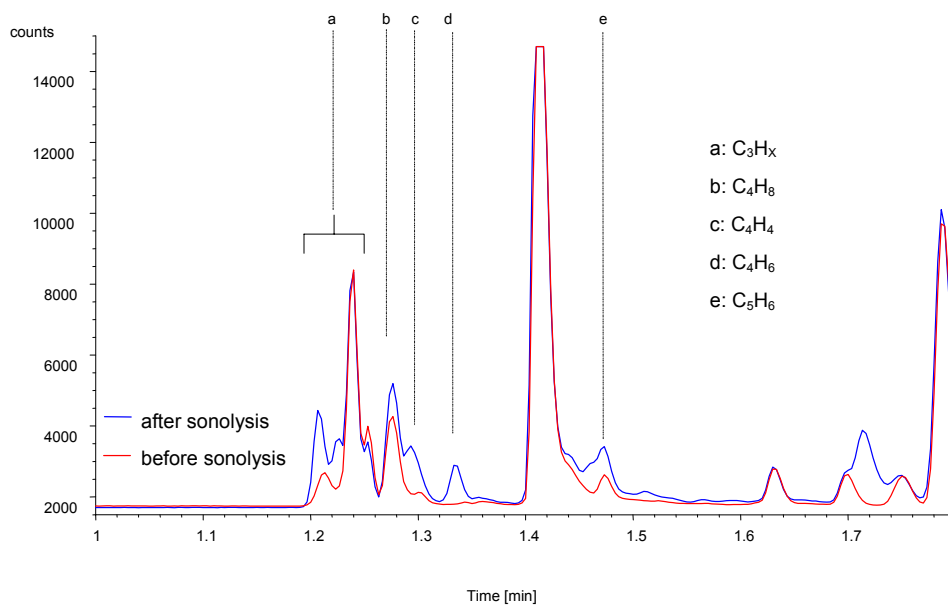


Figure 5-2 Gas chromatography of products from the sonolysis of 2-hexyne

(GC conditions: column: HP-5; carried gas: H<sub>2</sub> (split injection); P: 3 Psi; T<sub>c</sub>: 35 °C; T<sub>i</sub>: 250 °C; T<sub>d</sub>: 290 °C)

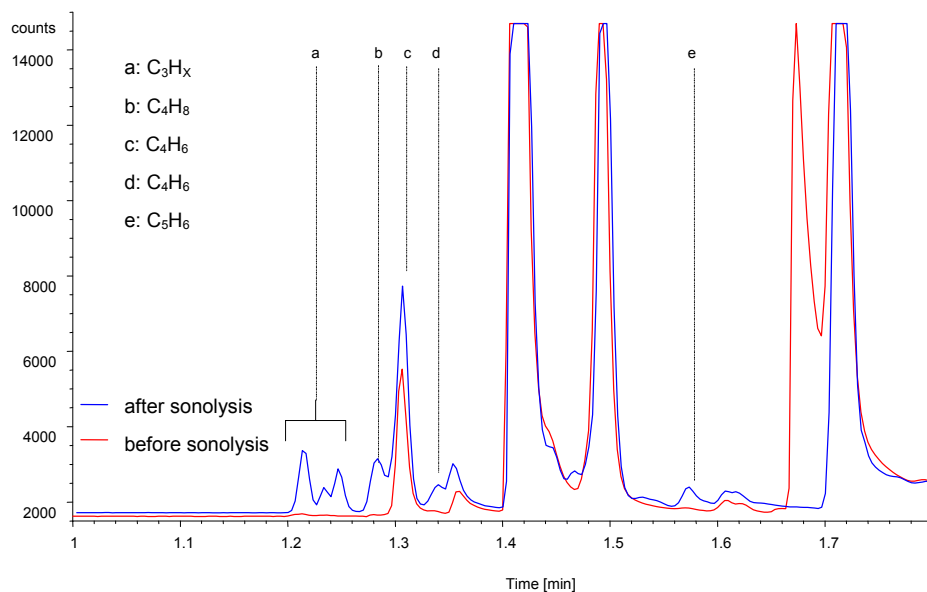


Figure 5-3 Gas chromatograms of products from sonolysis of 3-hexyne

(GC conditions: column: HP-5, carried gas: H<sub>2</sub> (split injection); P<sub>i</sub>: 3 Psi; T<sub>c</sub>: 35 °C; T<sub>i</sub>: 250 °C; T<sub>d</sub>: 290 °C)

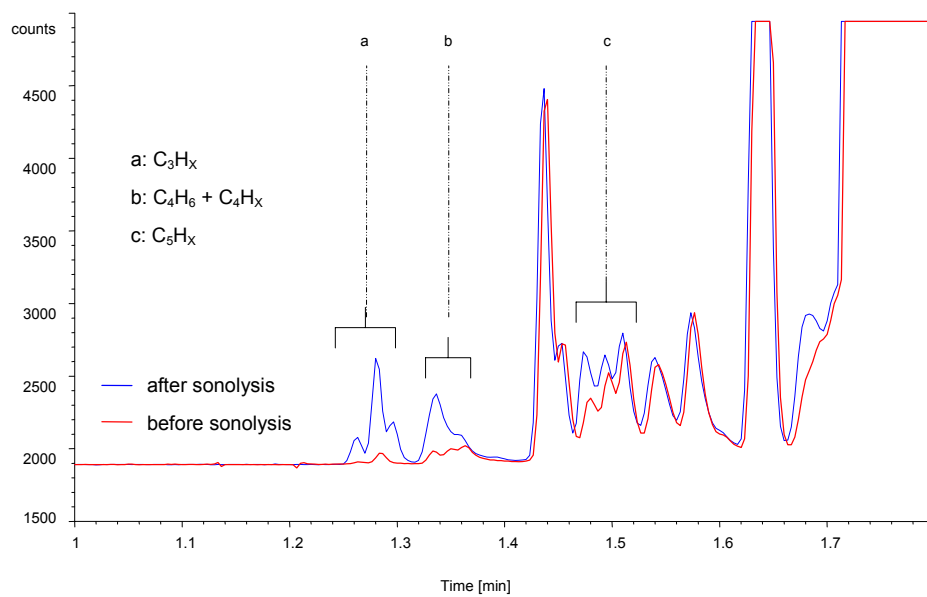


Figure 5-4 Gas chromatograms of products from sonolysis of 1,5-hexadiene

(GC conditions: column: HP-5, carried gas: H<sub>2</sub> (split injection); P<sub>i</sub>: 3 Psi; T<sub>c</sub>: 35 °C; T<sub>i</sub>: 250 °C; T<sub>d</sub>: 290 °C)

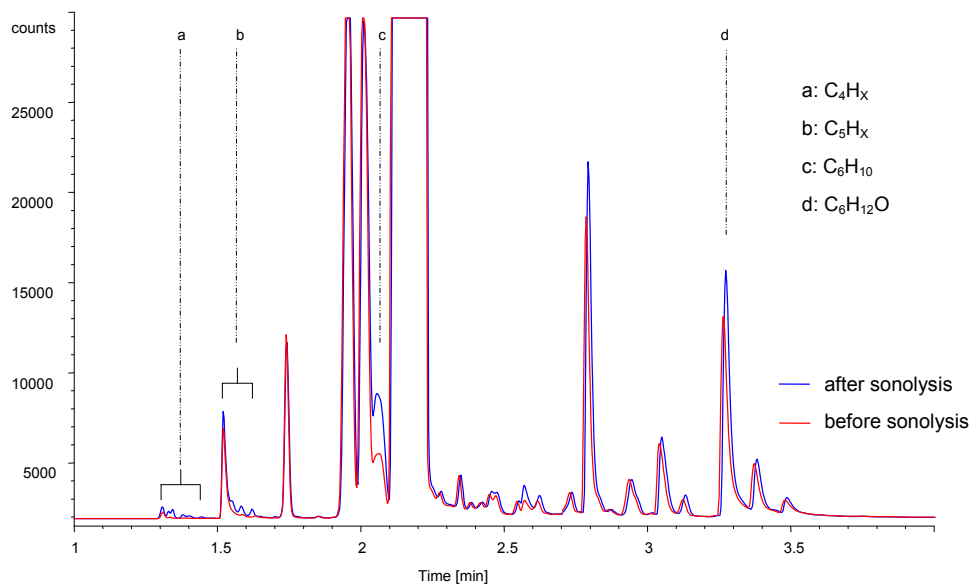
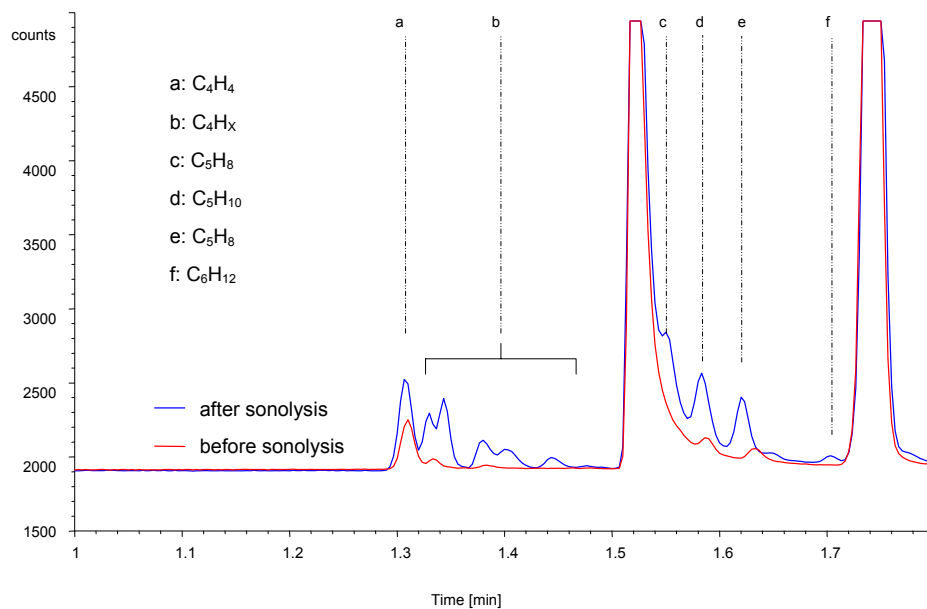
**(a) Formation of  $C_6$  species****(b) Formation of  $C_4$  and  $C_5$  species**

Figure 5-5 Gas chromatograms of products from sonolysis of 2,3-dimethyl-2-butene

(GC conditions: column: HP-5, carried gas:  $H_2$  (split injection);  $P_i$ : 3 Psi;  $T_c$ : 35 °C;  $T_i$ : 250 °C;  $T_d$ : 290 °C)



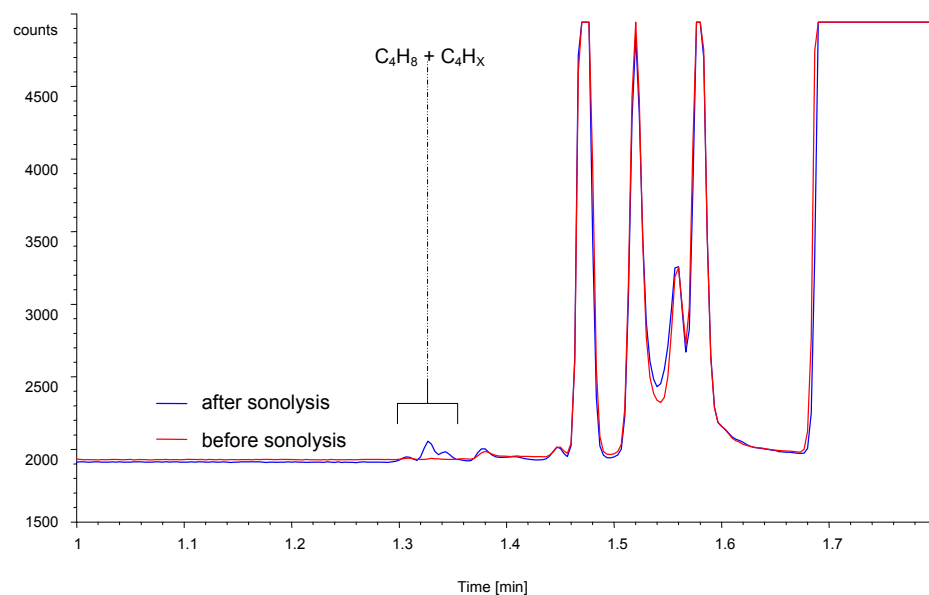


Figure 5-6 Gas chromatograms of products from sonolysis of 2,3-dimethyl-1-butene



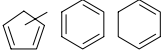


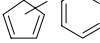



(GC conditions: column: HP-5, carried gas: H<sub>2</sub> (split injection); Pi: 3 Psi; Tc: 35 °C; Ti: 250 °C; Td: 290 °C)

### 5.1.3 Sonolyses of the Selected Cyclic C<sub>6</sub>H<sub>X</sub> Hydrocarbons at Low Temperature

The sonolytic products of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene in the cold media of a dry-ice/isopropanol mixture (208 K) were investigated. Ultrasonic frequency and intensity are 24 kHz and 45 W cm<sup>-2</sup> respectively. The irradiation volume and time are 2.5 mL and 4 h respectively. The ultrasonic irradiations were carried out in the atmosphere of dry-air. Table 5-3 shows the results by GC/MS analysis.

Table 5-3 Sonolytic products and pseudo-yields of the selected cyclic C<sub>6</sub>H<sub>X</sub> at low temperature

(24 kHz, 45 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h)

Substrates	Products				Phenomena	$\Delta_f H_{\text{gas}}^\circ$ [kJ mol <sup>-1</sup> ]	bp. [°C]	Pseudo- yield [%]
	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>				
cyclohexene	C <sub>3</sub> H <sub>X</sub> , 		C <sub>5</sub> H <sub>6</sub> , C <sub>5</sub> H <sub>8</sub>	C <sub>6</sub> H <sub>8</sub> , C <sub>6</sub> H <sub>10</sub> , 	Colorless to yellow liquid	-4.32	82.9	0.0561
1,3- cyclohexadiene	C <sub>3</sub> H <sub>X</sub> , 		C <sub>5</sub> H <sub>6</sub> , C <sub>5</sub> H <sub>8</sub> , C <sub>5</sub> H <sub>10</sub>		Colorless to yellow liquid	104.6	80.5	0.3752
1,4- cyclohexadiene	C <sub>3</sub> H <sub>X</sub> , 		C <sub>5</sub> H <sub>6</sub> , C <sub>5</sub> H <sub>8</sub>	C <sub>6</sub> H <sub>10</sub> , 	Colorless to yellow liquid	104.8	85.5	0.9621

Smaller molecules are also formed during sonolyses of the selected cyclic  $C_6H_X$  hydrocarbons at low temperature. There, the  $C_3$ ,  $C_4$ , and  $C_5$  species are generated from the cleavage of C-C bonds most often. Especially, benzene (from dehydrogenation) and other  $C_6$  species (from molecular rearrangement) are also generated. Figure 5-7 to Figure 5-9 illustrate the changes observed by GC, before and after sonolyses of the selected cyclic  $C_6H_X$  hydrocarbons.

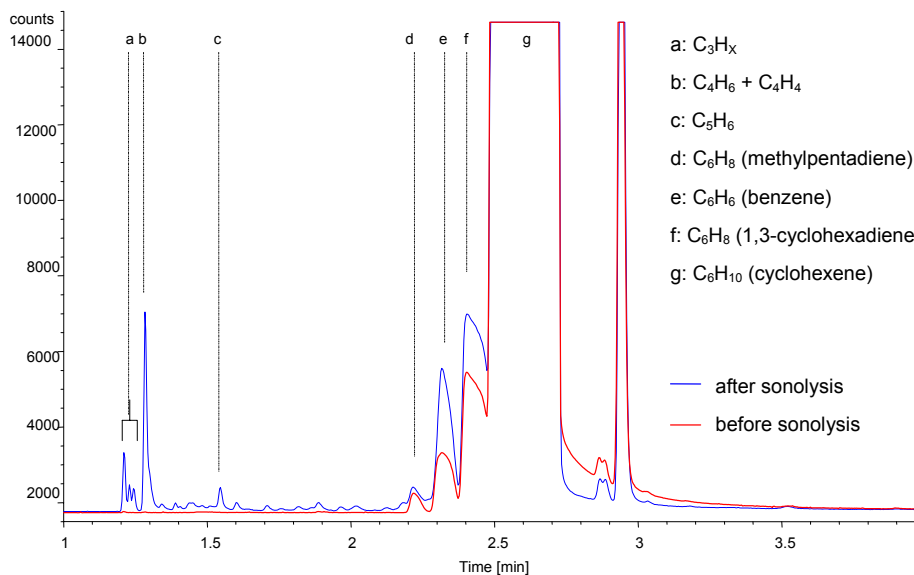


Figure 5-7 Gas chromatograms of products from the sonolysis of cyclohexene

(GC conditions: column: HP-5, carried gas:  $H_2$  (split injection); Pi: 3 Psi; Tc: 35 °C; Ti: 250 °C; Td: 290 °C)

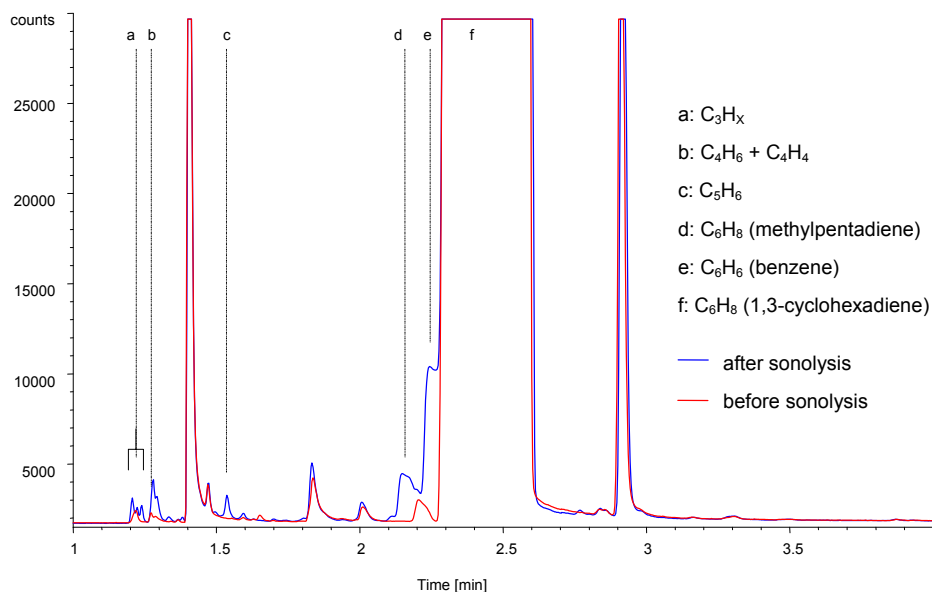


Figure 5-8 Gas chromatograms of products from sonolysis of 1,3-cyclohexadiene

(GC conditions: column: HP-5, carried gas:  $H_2$  (split injection); Pi: 3 Psi; Tc: 35 °C; Ti: 250 °C; Td: 290 °C)

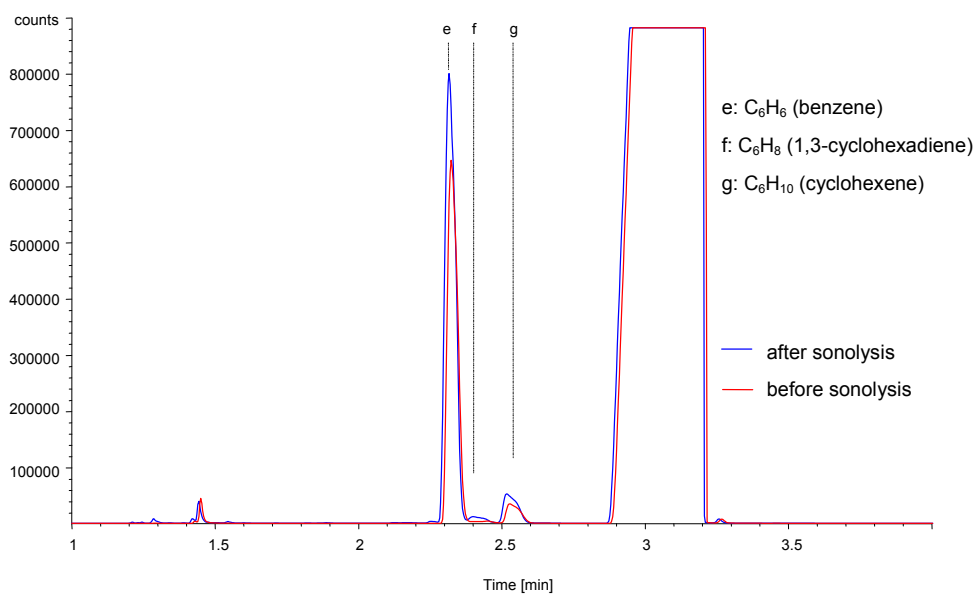
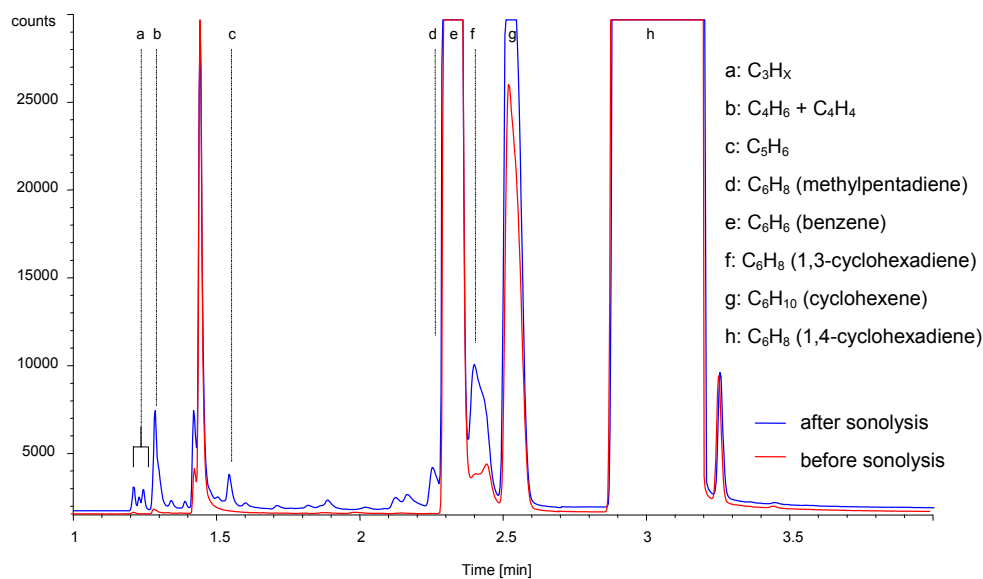
**(a) Formation of benzene****(b) Formations of C<sub>3</sub> – C<sub>5</sub> species**

Figure 5-9 Gas chromatograms of products from sonolysis of 1,4-cyclohexadiene

(GC conditions: column: HP-5, carried gas: H<sub>2</sub> (split injection); Pi: 3 Psi; Tc: 35 °C; Ti: 250 °C; Td: 290 °C)

In Chapter 4, C<sub>6</sub> products from aquasonolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene have been investigated in detail. In order to compare the mechanisms of the sonolysis in aqueous solutions with those occurring in nonaqueous liquids, C<sub>6</sub> products from sonolyses of pure liquids of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene at low temperature are investigated in detail.

GC response factors of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene were determined as to be 1.00, 1.12, 1.12, and 1.09 respectively. Concentrations of the unknown  $C_6H_8$  were calculated based on GC response factors of cyclohexadiene.

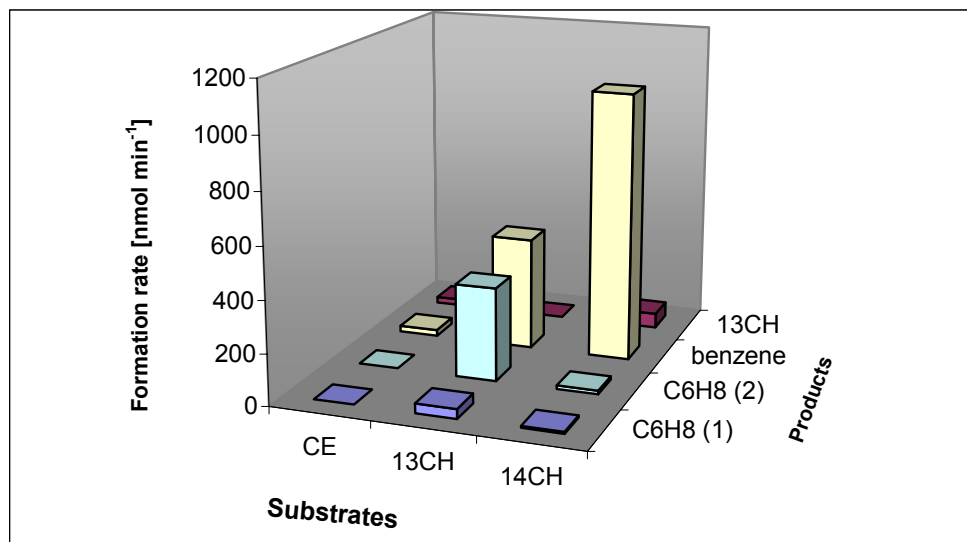


Figure 5-10 Formation rates of  $C_6$  products from sonolyses of CE, 13CH, and 14CH (24 kHz, 45 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h, CE: cyclohexene; 13CH: 1,3-cyclohexadiene; 14CH: 1,4-cyclohexadiene.)

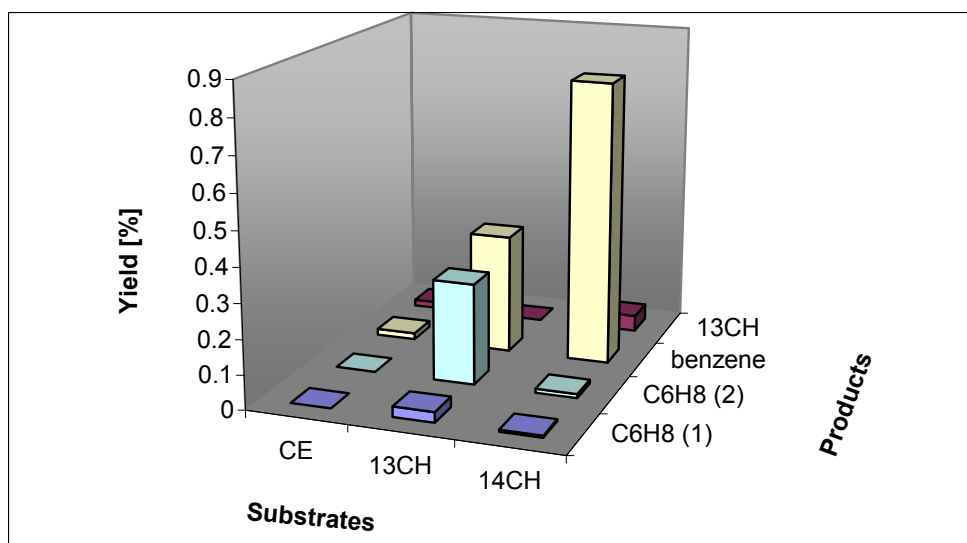


Figure 5-11 Yields of  $C_6$  products from sonolyses of CE, 13CH, and 14CH (24 kHz, 45 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h, CE: cyclohexene; 13CH: 1,3-cyclohexadiene; 14CH: 1,4-cyclohexadiene.)

Figure 5-10 and Figure 5-11 show formation rates and yields of methylcyclopentadienes and benzene from sonolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene respectively. The components of  $C_6$  products from sonolyses are similar to those from their aquasonolyses. Based on the formation rates and yields of  $C_6$  products, benzene is the major  $C_6$  product from the

sonolysis of 1,4-cyclohexadiene as compared with that from the sonolysis of 1,3-cyclohexadiene. Formation rates and yields of methylcyclopentadienes from the sonolysis of 1,3-cyclohexadiene are very similar to those of benzene. Hence, the thermal dehydrogenation of 1,4-cyclohexadiene dominates its sonolysis, and the thermal dehydrogenation and the cleavage of C-C bonds occur simultaneously. Although formation rates and yields of benzene and 1,3-cyclohexadiene from the sonolysis of cyclohexene are very low, the cyclohexene also undergoes the thermal dehydrogenation by ultrasonic irradiation at low temperature.

## **5.2 Sonolytic Products of Selected Cyclic C<sub>6</sub>H<sub>X</sub> Hydrocarbons in Nonaqueous Solutions**

Due to their low vapor pressures, n-propanol, n-decane, and tetrachloroethylene can be sonolyzed at room temperature (298 K) [41, 42, 142]. Therefore, the above-mentioned liquids can be used as solvents for sonolyses of unsaturated C<sub>6</sub>-hydrocarbons. Sonolytic rates and products of benzene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, cyclohexene, and cyclohexane in organic solvents at normal temperature (291 K) are studied in this work.

### **5.2.1 Formation of Benzene during Sonolyses of Cyclohexene and Cyclohexadiene in Organic Solvents**

Benzene is formed as the typical product from aquasonolyses of the selected C<sub>6</sub>H<sub>X</sub> hydrocarbons [168]. Likewise, benzene can be observed, if sonolyses of the selected C<sub>6</sub>H<sub>X</sub> hydrocarbons are carried out in organic solvents. Figure 5-12 shows yield changes of benzene with sonication time during sonolyses of cyclohexene and cyclohexadiene in tetrachloroethylene. GC response factors of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene are determined as to be 1.00, 1.12, 1.12, and 1.09 respectively.

Obviously, the yield of benzene from 1,3-cyclohexadiene is greater than that from 1,4-cyclohexadiene, consistent with their sonolytic rates (see Section 6.3). Since the vapor pressure of 1,3-cyclohexadiene is higher than that of 1,4-cyclohexadiene, it may be easier for the former to transfer into the cavitation bubbles from the surrounding tetrachloroethylene.

Figure 5-13 shows yield changes of benzene with sonication time during the sonolysis of 1,3-cyclohexadiene in different solvents. The order of the yields is also consistent with the order of the sonolytic rates (see Section 6.3). It may have a higher collapse temperature of the cavitation bubbles in tetrachloroethylene than in other solvents. In other words, under reaction conditions

investigated here, the Woodward-Hoffmann-rule of thumb (molecular 1,4-hydrogen elimination!) seems evidently to fail.

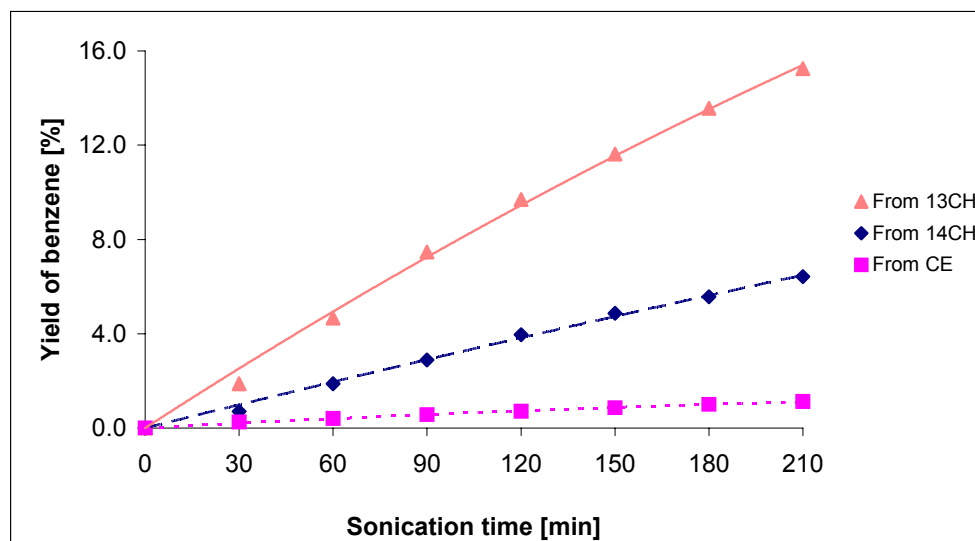


Figure 5-12 Yields of benzene during sonolyses of CE, 13CH, and 14CH in TCE (33.3 mmol L<sup>-1</sup> solution, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K, 13CH: 1,3-cyclohexadiene; 14CH: 1,4-cyclohexadiene; CE: cyclohexene; TCE: tetrachloroethylene)

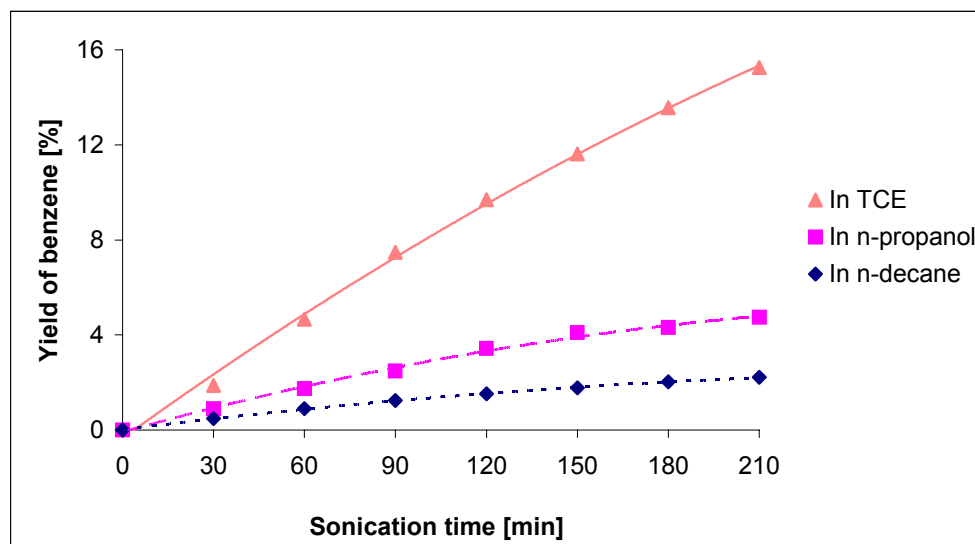


Figure 5-13 Yields of benzene during sonolyses of 13CH in different solvents (33.3 mmol L<sup>-1</sup> solution, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K, 13CH: 1,3-cyclohexadiene; TCE: tetrachloroethylene.)

### 5.2.2 Secondary Reactions Occurring during Sonolyses of Cyclohexene and Cyclohexadiene in Tetrachloroethylene

Tetrachloroethylene is partly instable under investigated sonolytic conditions, therefore decomposition products such as chlorine, chlorine atoms, and chlorinated radicals are released into the bulk liquid, where these intermediates react with double bonds. Figure 5-14 shows the yield changes of dichlorinated compounds generated by a complex reaction mechanism. Since vapor pressures of 1,4-cyclohexadiene and cyclohexene are lower than 1,3-cyclohexadiene, they may be more difficult to transfer into the cavitation bubbles. Thus, the yields of dichlorinated compounds from 1,4-cyclohexadiene and cyclohexene are higher.

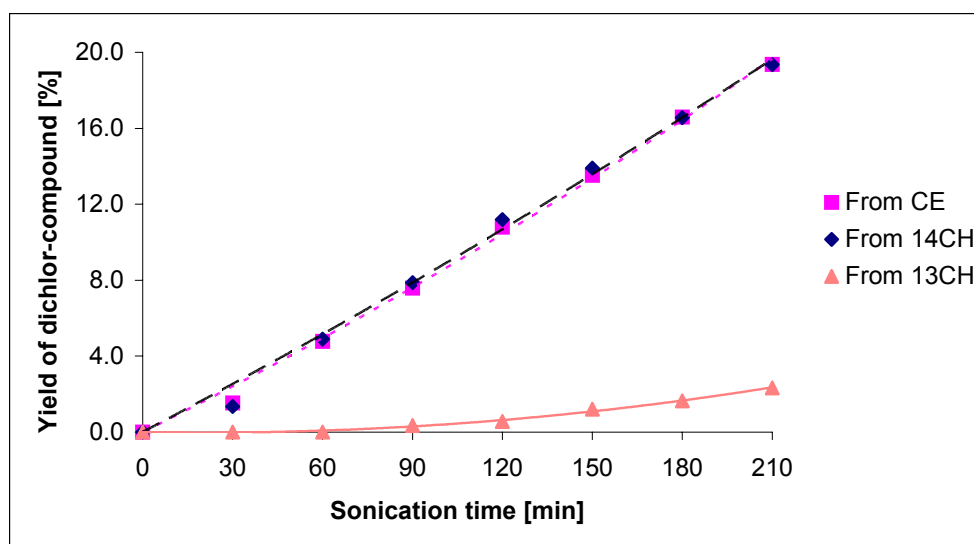


Figure 5-14 Yields of Cl-compounds during sonolyses of CE, 13CH, and 14CH in TCE (Ultrasonic conditions: 33.3 mmol L<sup>-1</sup> solution, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K. 13CH: 1,3-cyclohexadiene; 14CH: 1,4-cyclohexadiene; CE: cyclohexene; TCE: tetrachloroethylene)

### 5.2.3 Secondary Reactions Occurring during Sonolyses of Benzene and Cyclohexane in Tetrachloroethylene

Under ultrasonic irradiation, benzene reacts to yield chlorobenzene in tetrachloroethylene in the presence of FeCl<sub>3</sub>. Figure 5-15 shows that pseudo-first-order rate constant in presence of FeCl<sub>3</sub> is over 3 times higher than in the absence of FeCl<sub>3</sub>. It is assumed that chlorine, chlorine atoms, and chlorinated radicals are firstly released during the sonolysis of tetrachloroethylene [142], then the chlorination of benzene takes place in the bulk liquid. It is further derived that the transfer of benzene from the organic bulk liquid into the cavitation bubbles is very difficult. Obviously, it should further be investigated which is the major pathway of chlorination, electrophilic substitution or free radical reaction.

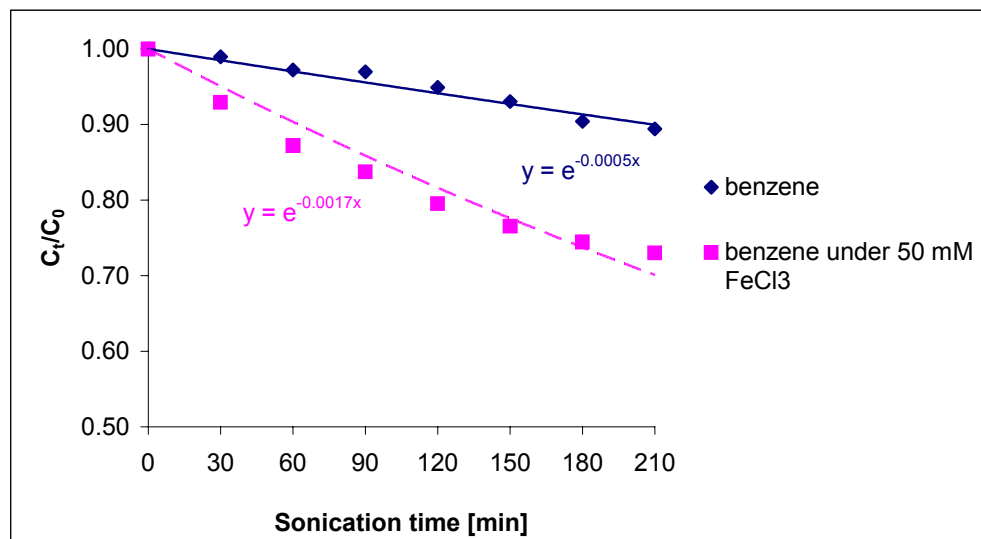


Figure 5-15 Effect of  $FeCl_3$  on the sonolytic rates of benzene in tetrachloroethylene  
(33.3 mmol L<sup>-1</sup> solution, 50.0 mmol L<sup>-1</sup>  $FeCl_3$ , 20 mL, 24 kHz, 45W cm<sup>-2</sup>, 291 K)

In general, cycloalkanes are able to react with chlorine under the influence of light, heat or a catalyst [174]. Similarly, chlorocyclohexane is produced during the sonolysis of cyclohexane in tetrachloroethylene. Figure 5-16 shows yield changes of chlorobenzene and chlorocyclohexane with sonication time during sonolyses of benzene and cyclohexane in tetrachloroethylene.

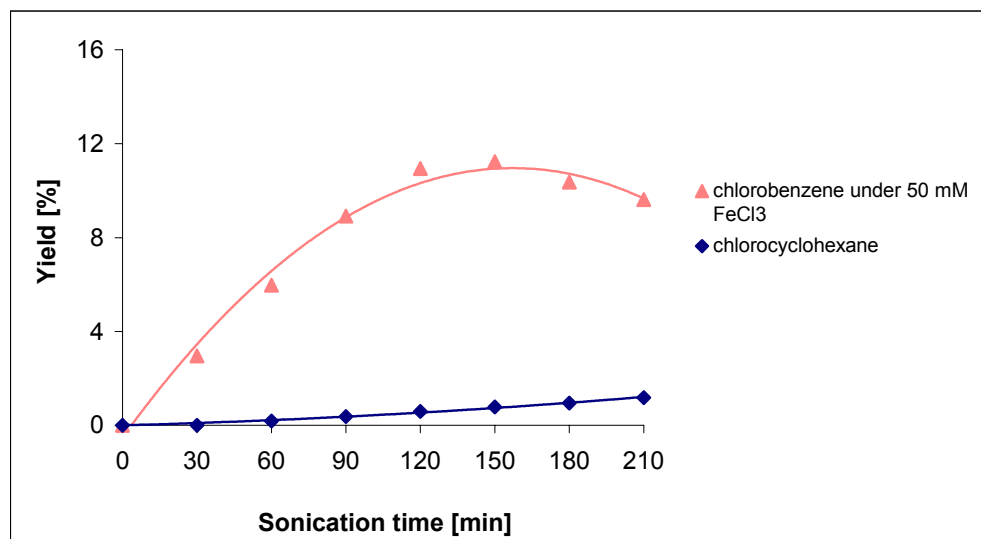


Figure 5-16 Yield changes of chlorinated products from sonolyses of Ben and CA in TCE  
(33.3 mmol L<sup>-1</sup>, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K; chlorobenzene produced under the catalysis of 50 mmol L<sup>-1</sup>  $FeCl_3$ ,

Ben: benzene; CA: cyclohexane; TCE: tetrachloroethylene)



### 5.3 Sonolytic Products of Pure Thioethers

Sonolyses of aliphatic, aromatic, and naphthenic hydrocarbons, and  $\text{BrCCl}_3$  have been reported [41, 43, 142, 144, 146]. A decreasing vapor pressure of the solvent increases the intensity of cavitation collapse, the maximum temperature of the collapse, and the rates of sonochemical reactions. The ultrasound-induced cracking of organic compounds is quite similar to very high temperature pyrolysis.

In this work, the rates of DPPH trapping, sonolytic products, and the effect of operational temperature, vapor pressure, and ultrasonic intensity on sonolyses of thioethers were investigated.



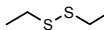
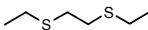
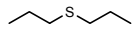


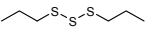
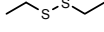
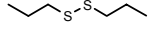


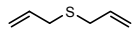
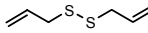
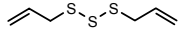

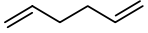
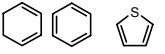
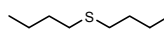

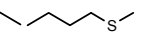
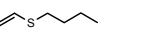



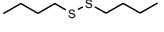
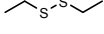
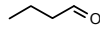
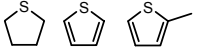
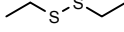

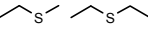
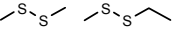
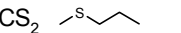
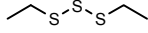


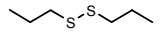

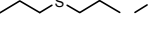


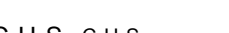
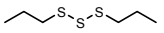

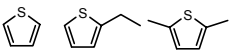
The ultrasonic processor worked at 24 kHz under the atmosphere of dry-air. The ultrasonic intensity determined by calorimetric measurement can be regulated ( $15\text{--}45 \text{ W cm}^{-2}$ ). The temperature of the bulk liquid in the reactor was maintained at normal temperature (283 K) by circulating cooling water (278 K), or low temperature (208 K) by the mixture of dry-ice and isopropanol. The volume of each sample irradiated was 3 mL.

It has been reported that  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{H}_2$  can be formed during pyrolyses of methyl benzyl sulfide ( $\text{CH}_3\text{SCH}_2\text{Ph}$ ), dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ ), dimethyl disulfide ( $\text{CH}_3\text{SSCH}_3$ ) [171]. Due to the higher vapor pressure of dimethyl sulfide, no product was found from dimethyl sulfide during the ultrasonic irradiation at normal temperature. However, other sulfides and disulfides can undergo sonolysis at normal temperature, although yields are relatively low. At low temperature, yields of most products increased greatly.

Table 5-4 shows the sonolytic products of thioethers at low temperatures. In term of Table 5-4,  $\text{CS}_2$ , smaller sulfides, and sulfurized species are the most common sulfur-containing products occurred by the cleavage of bonds. Disulfides or trisulfides can readily be formed during sonolyses of sulfides or disulfides. Thiophene, thiols, and hydrocarbons are also formed from thioethers during ultrasonic irradiation. Especially, more hydrocarbons are produced during the sonolysis of diallyl sulfide, such as 1,5-hexadiene, 1,3-cyclohexadiene, and benzene. Also, some oxidized products are detected, e.g.,  $\text{SO}_2$  and aldehydes. All products demonstrate that thioethers undergo pyrolyses and complex radical reactions during ultrasonic irradiation.

In order to elucidate the enhanced effect of low temperature (i.e., low vapor pressure of solvent) on the formation of products, the enhancement factors of low temperature are calculated using equation (E5-2), and the results are listed in Table 5-5.

Table 5-4 Products from sonolyses of thioethers at low temperature  
(3 mL, 24 kHz, 30 W cm<sup>-2</sup>, 208 K, 4 h sonication)

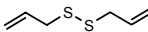
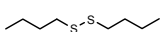
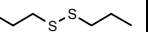
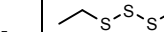
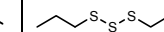
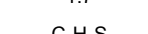
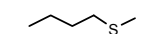
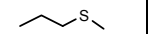
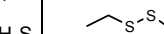
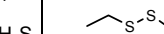
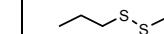
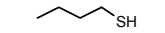
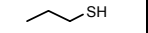
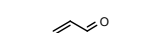
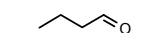
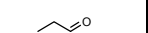
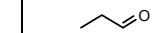
Substrates	Cleavage of bonds	Sulfurized	Oxidized	Other radical reaction
DES, C <sub>4</sub> H <sub>10</sub> S 	CS <sub>2</sub> 		SO <sub>2</sub>	
DPS, C <sub>6</sub> H <sub>14</sub> S 	CS <sub>2</sub>  C <sub>3</sub> H <sub>6</sub> S 	  	SO <sub>2</sub> 	 C <sub>5</sub> H <sub>10</sub> S
DAS, C <sub>6</sub> H <sub>10</sub> S 	CS <sub>2</sub> C <sub>3</sub> H <sub>6</sub> S	  C <sub>4</sub> H <sub>10</sub> S <sub>2</sub> C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> C <sub>6</sub> H <sub>8</sub> S <sub>2</sub>	SO <sub>2</sub>  C <sub>5</sub> H <sub>8</sub> O	C <sub>4</sub> H <sub>6</sub> C <sub>4</sub> H <sub>4</sub> C <sub>4</sub> H <sub>2</sub> C <sub>5</sub> H <sub>6</sub> C <sub>5</sub> H <sub>8</sub> C <sub>6</sub> H <sub>8</sub> C <sub>7</sub> H <sub>12</sub>   C <sub>5</sub> H <sub>8</sub> S C <sub>6</sub> H <sub>10</sub> S C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>
DBS, C <sub>8</sub> H <sub>18</sub> S 	CS <sub>2</sub>      	 	SO <sub>2</sub> 	
DEDS, C <sub>4</sub> H <sub>10</sub> S <sub>2</sub> 	CS <sub>2</sub>    	 C <sub>4</sub> H <sub>10</sub> S <sub>4</sub>	SO <sub>2</sub> 	C <sub>4</sub> H <sub>6</sub> C <sub>4</sub> H <sub>4</sub>  S <sub>8</sub> C <sub>4</sub> H <sub>8</sub> S C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> C <sub>5</sub> H <sub>12</sub> S <sub>2</sub>
DPDS, C <sub>6</sub> H <sub>14</sub> S <sub>2</sub> 	CS <sub>2</sub>      C <sub>3</sub> H <sub>6</sub> S C <sub>3</sub> H <sub>6</sub> S <sub>2</sub>	 C <sub>2</sub> H <sub>2</sub> S <sub>4</sub> C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	SO <sub>2</sub> 	C <sub>4</sub> H <sub>6</sub> C <sub>6</sub> H <sub>10</sub> C <sub>6</sub> H <sub>12</sub> C <sub>6</sub> H <sub>14</sub> C <sub>5</sub> H <sub>10</sub> S C <sub>5</sub> H <sub>12</sub> S  C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> C <sub>6</sub> H <sub>12</sub> S S <sub>8</sub>

$$F_e = \frac{(A_{it} - A_{i0})/t_i}{(A_{rt} - A_{r0})/t_r} \quad (E\ 5-2)$$

where  $A_{it}$  is the GC peak area of a selected product at a given reaction time at 208 K,  $A_{i0}$  is the GC peak area of a selected product at the initial time at 208 K,  $t_i$  is the reaction time at 208 K,  $A_{rt}$  is the

GC peak area of a selected product at a given reaction time at 283 K,  $A_{r0}$  is the GC peak area of a selected product at the initial time at 283 K,  $t_r$  is the reaction time at 283 K.

Table 5-5 Enhancement factors of the low temperature on the formation of typical products  
(3 mL, 24 kHz, 30 W cm<sup>-2</sup>, 4 h sonication at 208 and 283 K respectively)

Substrates	DAS	DBS	DPS	DES	DEDS	DPDS
Sulfurized species	0.9 	+ 	0.3 	-	0.7 	0.4 
Small sulfides	1.7 C <sub>3</sub> H <sub>6</sub> S 	+ 	+ 	+ C <sub>2</sub> H <sub>4</sub> S 	0.8 	0.9 
Thiols	-	+ 	47.6 	-	-	-
CS <sub>2</sub>	+	+	106.5	+	2	2.8
Thiophene	+	+	+	-	+	1.8
Aldehydes	2.8 	1.0 	+ 	-	-	1.2 
SO <sub>2</sub>	+	+	+	+	+	+
S <sub>8</sub>	-	-	-	-	5.3	3.1

Note:  $F_{>1}$ : enhanced effect, -: no detectable product at 208 and 283 K, +: detectable product only at 208 K.

According to Table 5-5, a reduced temperature enhances the cleavage of C-C and C-S bonds, and increases the yields of small sulfides, thiols, CS<sub>2</sub>, thiophene, oxidized products, and S<sub>8</sub> as well. Especially SO<sub>2</sub>, CS<sub>2</sub>, and thiophene are exclusively generated at low temperature. This demonstrates the enhancement effect of low temperature. However, yields of sulfurized products cannot be enhanced by low temperature. Since the C-S bond is the weakest bond within thioether molecules [175], and most thioethers have relatively low vapor pressures at normal temperature, the maximum collapse temperature may be high enough for the dissociation of C-S bonds at normal temperature.

## 5.4 Sonolytic Products of Pure Thiophene and Its Derivatives















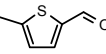
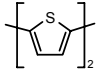






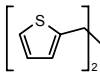

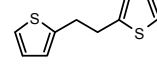
The ultrasonic processor worked at 24 kHz under the atmosphere of dry-air. The ultrasonic intensity determined by caloric measurement was 30 W cm<sup>-2</sup>. The tip diameter of the ultrasonic horn was 7 mm. The temperature of the bulk liquid in the reactor was maintained 283 K by circulating cooling water (278 K), or low temperature (208 K) by the mixture of dry-ice and isopropanol (208 K). The volume of each sample irradiated was 3 mL.

It has been reported that H<sub>2</sub>S, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> can be formed during the pyrolysis of thiophene [165-167]. Since the small species (< C<sub>4</sub>) cannot be detected by our sample method and HP-5MS GC-columns, heavier species were considered in this work.

No product was found from sonolyses of thiophenes at normal temperature. However, at low temperature, many products generated during sonolyses of thiophenes were found. Table 5-6 shows the sonolytic products of thiophenes and reaction phenomena at low temperature. Figure 5-17 to Figure 5-20 illustrate the changes observed by GC, before and after sonolyses of thiophenes at low temperature.

Table 5-6 Very volatile products from sonolyses of thiophene and its derivatives

(24 kHz, 30 W cm<sup>-2</sup>, 3 mL)

Substrate	S-containing products	S-free products			Oxidized products	Dimer	Others	Phenomenon	
		C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>				283 K	208 K
TH C <sub>4</sub> H <sub>4</sub> S 	CS <sub>2</sub> 	C <sub>4</sub> H <sub>2</sub> C <sub>4</sub> H <sub>4</sub>			SO <sub>2</sub>			Colorless liquid	Deeply brown liquid with many deposits
MTH C <sub>5</sub> H <sub>6</sub> S 	CS <sub>2</sub> 	C <sub>4</sub> H <sub>2</sub> C <sub>4</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>4</sub> C <sub>5</sub> H <sub>6</sub>	 C <sub>6</sub> H <sub>6</sub>	COS 		 	Colorless liquid	Deeply yellow liquid with many deposits
DMTH C <sub>6</sub> H <sub>8</sub> S 	CS <sub>2</sub>  	C <sub>4</sub> H <sub>2</sub> C <sub>4</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>4</sub>		COS  		C <sub>7</sub> H <sub>10</sub> S	4 h, very slight yellow liquid, no deposits	4 h Deeply yellow liquid with deposits
ETH C <sub>6</sub> H <sub>8</sub> S 	CS <sub>2</sub>  	C <sub>4</sub> H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> C <sub>4</sub> H <sub>6</sub>	C <sub>5</sub> H <sub>4</sub> C <sub>5</sub> H <sub>6</sub>	 C <sub>6</sub> H <sub>6</sub>	COS   C <sub>6</sub> H <sub>6</sub> OS, C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> S, C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> S		  C <sub>6</sub> H <sub>4</sub> S, C <sub>7</sub> H <sub>10</sub> S, C <sub>8</sub> H <sub>12</sub> S, C <sub>11</sub> H <sub>12</sub> S <sub>2</sub> , C <sub>12</sub> H <sub>14</sub> S <sub>2</sub> , C <sub>13</sub> H <sub>16</sub> S <sub>2</sub>	6 h, yellow liquid, no deposits	6 h Deeply yellow liquid with deposits

At low temperature, ultrasonic irradiation of thiophenes causes a darkening of color from colorless or slight yellow liquids to deeply yellow with a few brown deposits. CS<sub>2</sub>, dimer, and thiophene, formed by the cleavage of alkyls, are the most common sulfur-containing products. C<sub>4</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>4</sub>,

$C_5H_4$ ,  $C_5H_6$ , and  $C_6H_6$  are the common hydrocarbons. Meanwhile, some oxidized products are detected, i.e.,  $SO_2$ , COS, furan, and aldehydes. All of these products demonstrate that thiophene and its derivatives undergo pyrolyses and complex radical reactions during the ultrasonic irradiation.

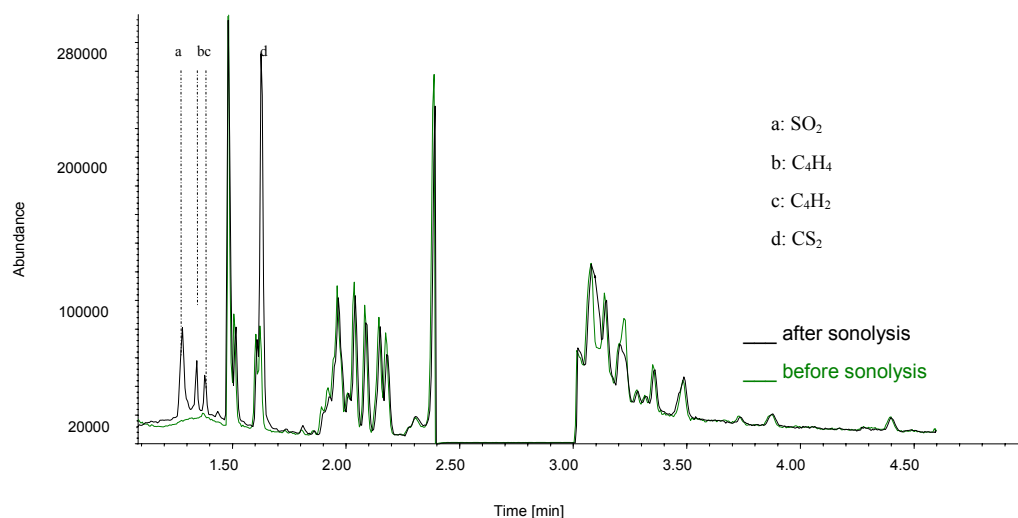


Figure 5-17 Gas chromatograms of products from the sonolysis of thiophene

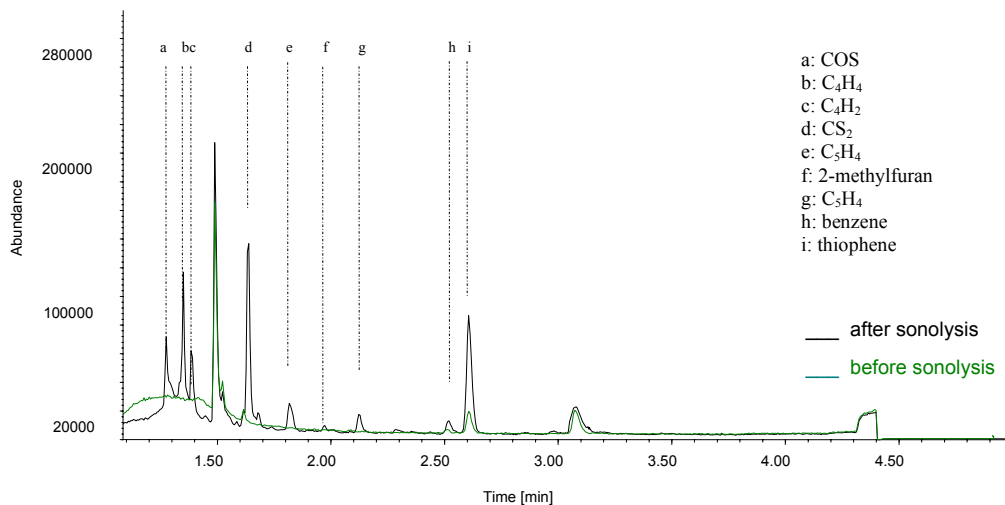


Figure 5-18 Gas chromatograms of products from the sonolysis of 2-methylthiophene

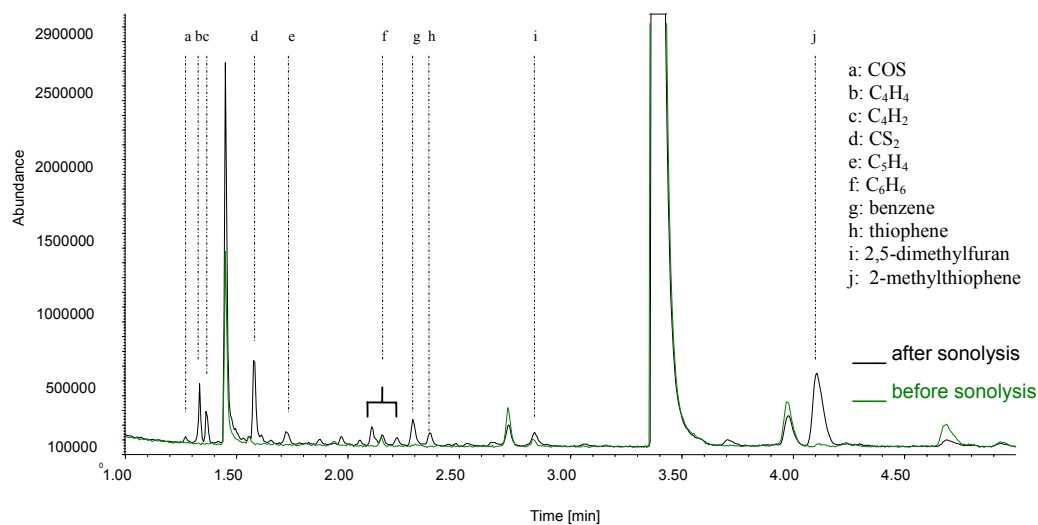


Figure 5-19 Gas chromatograms of products from the sonolysis of 2,5-dimethylthiophene

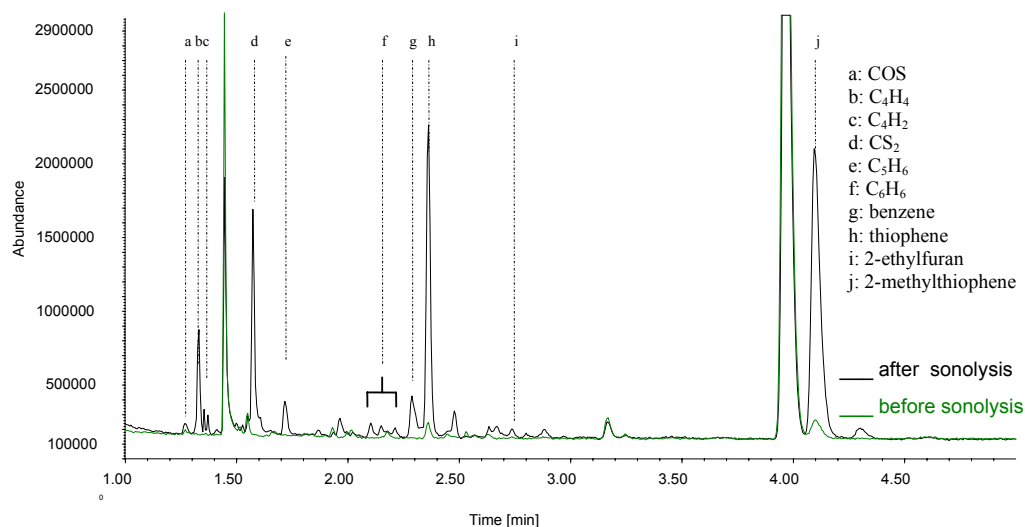


Figure 5-20 Gas chromatograms of products from the sonolysis of 2-ethylthiophene

## 5.5 Sonolytic Products of N-Heterocycles

The thermal rearrangement of N-methylpyrrole to 2-methylpyrrole at 823-923 K has been reported in 1962 [176]. In addition, small amounts (2-5%) of pyrrole and pyridine were obtained at 923 K. Lifshitz et al. [177] demonstrated the isomerization by the thermal decomposition of N-methylpyrrole. In addition, N-containing species such as HCN, CH<sub>3</sub>CN, CH<sub>2</sub>=CH-CN, C<sub>2</sub>H<sub>5</sub>CN,

and  $\text{CH}_3\text{CH}=\text{CHCN}$  were observed. Also, a number of hydrocarbons such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_3\text{H}_4$  were found.


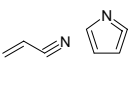



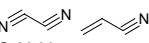


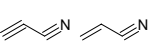


The thermal decomposition of pyrrole at a temperature range of 1050 -1450 K was reported in 1989 [178]. N-containing products are  $\text{CH}_3\text{CH}=\text{CHCN}$ ,  $\text{HCN}$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{CN}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2=\text{CHCN}$ ,  $\text{HCCCN}$ , etc. N-free products are  $\text{CH}_3\text{CCH}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_2=\text{C}=\text{CH}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_4\text{H}_6$ ,  $\text{C}_4\text{H}_4$ ,  $\text{C}_4\text{H}_2$ ,  $\text{C}_6\text{H}_6$ .

Products from the pyrolysis at 1371-1396 K of pyridine include quinoline, benzonitrile ( $\text{C}_6\text{H}_5\text{CN}$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ), 2-propenenitrile ( $\text{H}_2\text{C}=\text{CHCN}$ ), and benzene [179]. Mackie [180] found that cyanoacetylene is the principal N-containing product at 1300 K and hydrogen cyanide predominates at elevated temperature (1800 K). Other major products are  $\text{H}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HCCCN}$ ,  $\text{C}_4\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_4\text{H}_4$ ,  $\text{CH}_4$ ,  $\text{PhCN}$ ,  $\text{H}_2\text{C}=\text{CHCN}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_3\text{H}_4$ , and  $\text{CH}_3\text{CN}$ .

In this work, sonolytic products of pyrrole, N-methylpyrrole, and pyridine in the cold media of dry-ice/isopropanol mixture (208 K) are investigated. Ultrasonic frequency and intensity are 24 kHz and  $30 \text{ W cm}^{-2}$  respectively. The irradiation volume and time are 2.5 mL and 4 h respectively. The ultrasonic irradiations were carried out in the atmosphere of dry-air. Table 5-7 shows the reaction phenomena, the pseudo-yield, and products identified by GC/MS analysis.

Table 5-7 Sonolytic products and pseudo-yields of the selected N-heterocycles

(24 kHz,  $30 \text{ W cm}^{-2}$ , 2.5 mL, 208 K, 4 h)

Substrates	N-containing products	N-free products			Oxidized products	Phenomena	Pseudo-yield [%]	
		C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>			208 K	283 K
N-methylpyrrole 			-	-		Deeply brown liquid became bright brown liquid in 4 h ultrasonic irradiation at low temperature.	0.0120	0
Pyridine 	 C <sub>4</sub> H <sub>2</sub> N <sub>2</sub>		C <sub>5</sub> H <sub>6</sub>		-	Colorless liquid became deeply brown liquid in 4 h ultrasonic irradiation at low temperature.	0.0151	0
Pyrrole 	 C <sub>4</sub> H <sub>5</sub> N		C <sub>5</sub> H <sub>6</sub> , C <sub>5</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>6</sub> , 	-	Deeply brown liquid became black liquid in 4 h ultrasonic irradiation at low temperature.	0.0531	0.0029

Since the small species, such as  $\text{HCN}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , etc., cannot be detected by our analytic methods (sample and GC-columns), heavier species were considered in this work. Based on Table 5-7, some very volatile species are formed during sonolyses of the selected N-heterocycles at low temperature. There, 2-propenenitrile ( $\text{H}_2\text{C}=\text{CHCN}$ ) and 1-buten-3-yne ( $\text{C}_4\text{H}_4$ ) generated from the cleavage of C-C and C-N bonds are the most common. In addition, pyrrole and furan is formed

during the sonolysis and oxidation of N-methylpyrrole, C<sub>5</sub> and C<sub>6</sub> species are formed during sonolyses of pyridine and pyrrole. Furthermore, products from radical recombination can also be observed, such as cyanogen (CNCN) from pyridine, and cyanoacetylene (HCCCN) from pyrrole. Figure 5-21 to Figure 5-23 illustrate the changes observed by GC, before and after sonolyses of the selected N-heterocycles.

These sonolytic products demonstrate that N-heterocycles undergo pyrolysis during the ultrasonic irradiation at low temperature. In the future, products from sonolyses of N-heterocycles should be further investigated, such as the sonochemical isomerization or rearrangement of N-methylpyrrole.

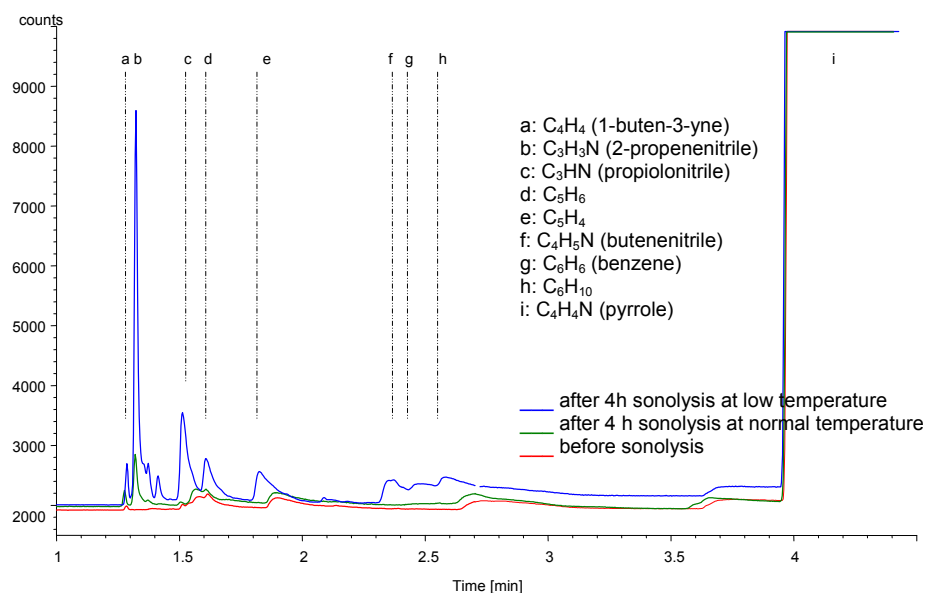


Figure 5-21 Gas chromatograms of products from the sonolysis of pyrrole



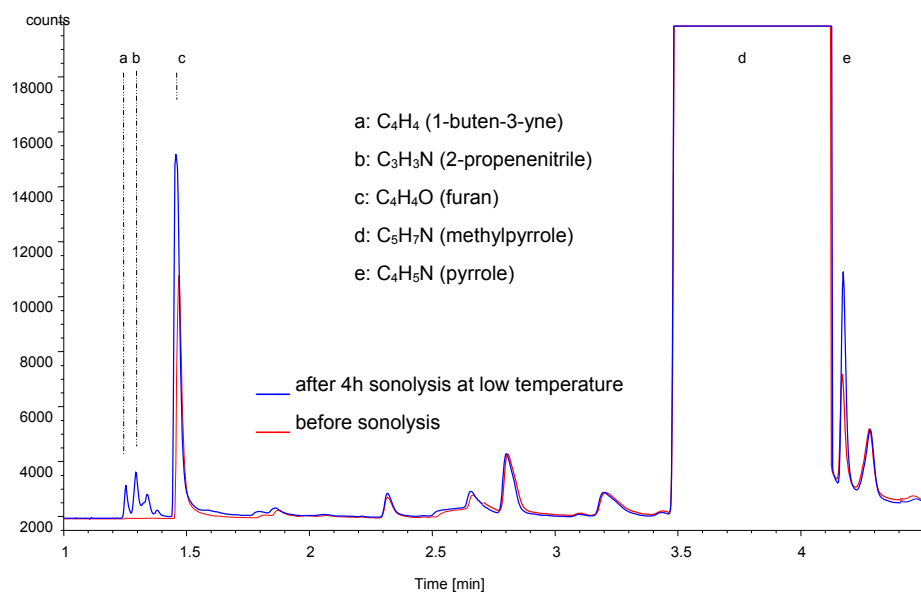


Figure 5-22 Gas chromatograms of products from the sonolysis of *N*-methylpyrrole

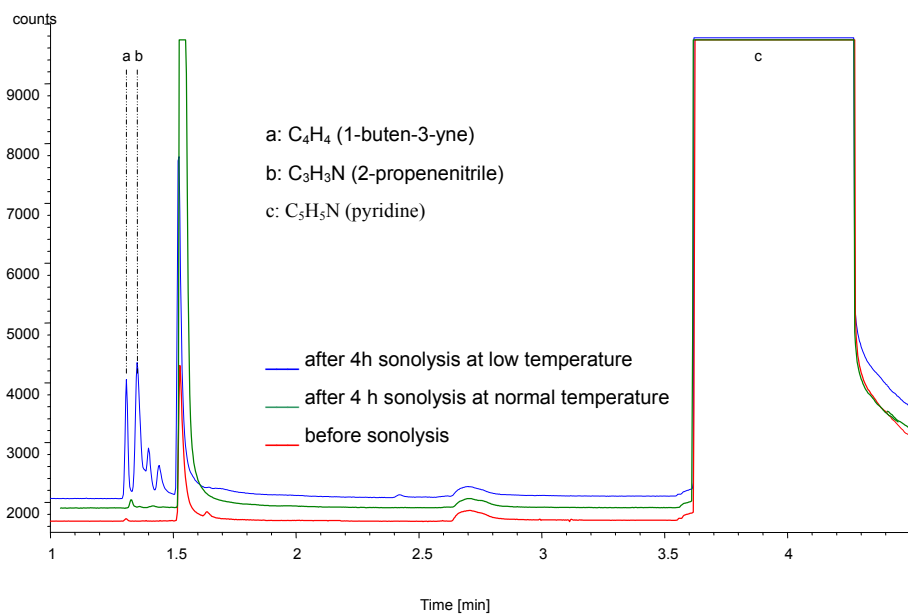


Figure 5-23 Gas chromatograms of products from the sonolysis of pyridine

## 6 Discussion

### 6.1 Sonolytic Kinetics in Aqueous Solutions

The volatilized loss of trichloroethylene, tetrachloroethylene, benzene and toluene during their sonochemical destruction had been observed by Kang et al. [79]. The volatilized loss was found to be less than 5%, which is a negligibly small to account for the kinetic consideration.

Though earlier investigators have stated a few influences of substrates, the mechanisms of aquasonolyses were not interpreted [19, 33-36]. In order to demonstrate the effect of the transfer processes of the organic substrates between cavitation bubbles and the bulk liquid on aquasonolyses of volatile organic substrates, the roles of thermostability, Henry's Law constants, volatility and hydrophobicity of substrates on aquasonolytic kinetics of cyclic and aliphatic C<sub>6</sub>H<sub>X</sub> hydrocarbons, thioethers, thiophenes, and N-heterocyclic compounds are investigated.

#### 6.1.1 Comparison of Aquasonolytic Rate Constants of Model Compounds

The aquasonolytic rate constants ( $k_{obs}$ ) determined are listed in Figure 6-1. The aquasonolytic rate constants show over a 90-fold variation at constant acoustic power intensity, frequency, and temperature.  $k_{obs}$  of 2,3-dimethyl-1-butene is the highest, and  $k_{obs}$  of pyridine is the lowest. In order to explain these results, their dependences on the relevant physicochemical properties are investigated.

#### 6.1.2 Roles of Thermostability of Organic Substrates

The physicochemical properties of a solute determine its capability to be sonicated. Since the pyrolyses of VOCs during the collapse of cavitation bubbles is generally regarded as the major pathway of sonolyses, the effects of the thermostability of the organic vapors on aquasonolyses of organic substrates are first concerned. The heat of formation ( $\Delta_f H^\circ_{gas}$ ) of compound is an important parameter of the thermostability. Based on gas phase thermochemistry data (see Table 3-1) [155], the relationship between the heats of formation and the aquasonolytic rate constants of the selected hydrocarbons are provided in Figure 6-2.

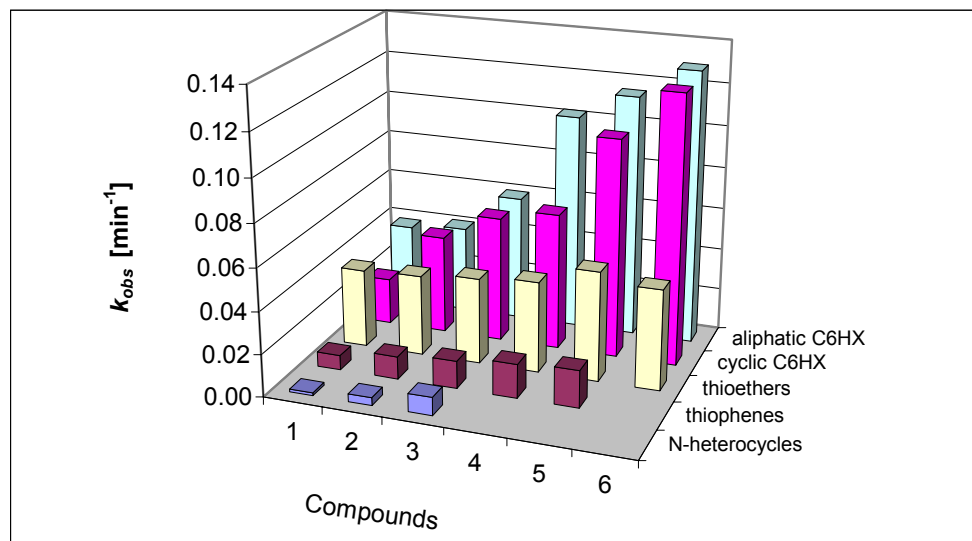


Figure 6-1 Aquasonolytic rate constants ( $k_{obs}$ ) of various organic substrates (500 mL, 850 kHz, 40 W, 295 K, 0.2 mmol L<sup>-1</sup> thioethers, 0.5 mmol L<sup>-1</sup> C<sub>6</sub>H<sub>x</sub>, 1.0 mmol L<sup>-1</sup> thiophenes, and 1.0 mmol L<sup>-1</sup> N-heterocycles, the numbers and names of compounds are noted in Table 3-1.)

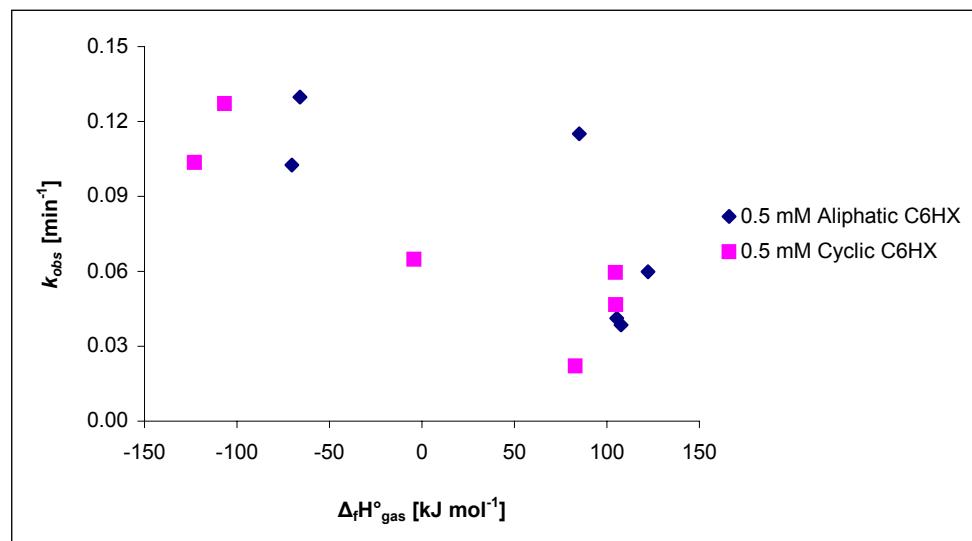


Figure 6-2  $\Delta_f H^\circ_{gas}$  versus  $k_{obs}$  of the selected hydrocarbons

Obviously, a higher heat of formation does not result in a higher aquasonolytic rate constant. Especially, methylcyclopentane and cyclohexane should be relatively thermostable, and difficult to convert by ultrasound. However, the aquasonolytic rates of methylcyclopentane and cyclohexane are relatively high, while the aquasonolytic rate of benzene is lower.

Similarly, the heat of formation of diethyl sulfide ( $-82.7 \text{ kJ mol}^{-1}$ ) is higher than that of dipropyl disulfide ( $-117.3 \text{ kJ mol}^{-1}$ ) [181, 182], indicating that dipropyl disulfide is more thermostable than diethyl sulfide, but dipropyl disulfide is sonicated faster than diethyl sulfide. In addition, the heat of

formation of thiophene (115 kJ mol<sup>-1</sup>) is higher than that of 2-methylthiophene (84.4 kJ mol<sup>-1</sup>) [155]. This shows that 2-methylthiophene is more thermostable than thiophene. However, 2-methylthiophene is sonicated faster than thiophene. The heat of formation of pyridine (140.7 kJ mol<sup>-1</sup>) is higher than that of pyrrole (108.3 kJ mol<sup>-1</sup>) [155], but pyrrole is sonicated much faster than pyridine.

Hence, the heat of formation does not evidently affect the aquasonolytic rates of organic substrates. In another word, the aquasonolytic rates of organic substrates are not directly related to their thermostability.

### 6.1.3 Roles of Henry's Law Constant and Transfer of Substrate

The Henry's Law constant ( $K_H$ ) characterizes the relative amount of a solute that will enter the vapor bubble, hence this parameter was investigated to identify the dependence of sonolysis [122, 183]. The Henry's Law constant of a compound, at its air-water distribution equilibrium, is defined as:

$$K_H = \frac{P_i}{C_w} \quad (E\ 6-1)$$

where  $K_H$  (kPa L mol<sup>-1</sup>) is the Henry's Law constant,  $P_i$  (kPa) is the partial pressure of the chemical species  $i$  in the gas phase, and  $C_w$  (mol L<sup>-1</sup>) is the aqueous phase concentration of the solute.

The Henry's Law constant is strongly associated with the transfer rates of the substrates from the bulk media to the cavities during the sonochemical destruction of trichloroethylene, tetrachloroethylene, benzene and toluene [79]. Due to a higher Henry's Law constant or higher vapor pressure, more CCl<sub>4</sub> diffuses into the bubbles and undergoes pyrolytic decomposition as the bubbles collapse than CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> [71]. The nonlinear relationships between the degradation rate constants and the Henry's Law constants of chlorinated methanes, ethanes, and ethenes have been shown in a scaled log-log plot [122].

Figure 6-3 shows the relationship between the aquasonolytic rate constants and the Henry's Law constants of various model compounds. Figure 6-4 shows the effects of the  $K_H$  on the aquasonolytic rate constants of the selected compounds under identical initial concentration.

Though some exceptional cases exist, a higher  $K_H$  generally results in a higher aquasonolytic rate constant. Hence, the transfer of the organic substrates between the bulk liquid and the cavitation bubbles is essential for the aquasonolysis.

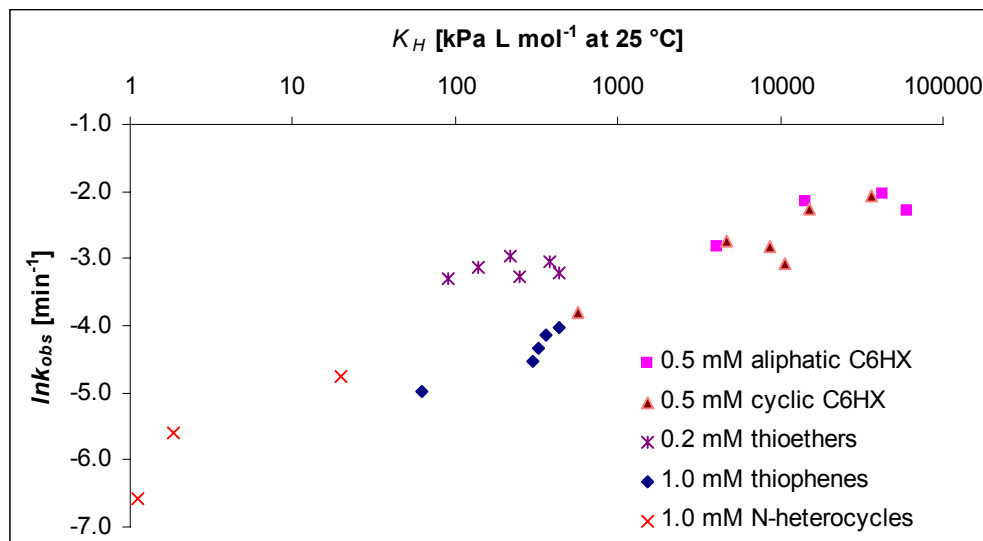


Figure 6-3  $k_{obs}$  versus  $K_H$  of substrates from various substrate groups  
(500 mL, 850 kHz, 40 W, 295 K)

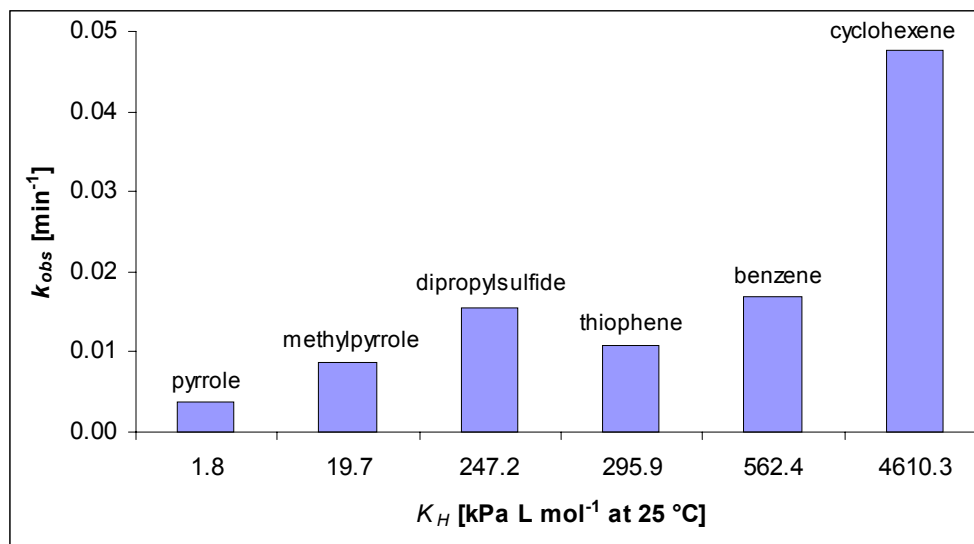


Figure 6-4 Effects of  $K_H$  of the selected substrates on  $k_{obs}$  under identical ultrasonic conditions  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

#### 6.1.4 Roles of Vapor Pressure of Substrate

Now that the transfer of the organic substrates between the bulk liquid and the cavitation bubbles is essential for the aquasonolysis, the effect of the volatility of the substrates on the aquasonolysis must be considered. Figure 6-5 shows the effects of the vapor pressure ( $P_V$ ) on the aquasonolytic rate constants of various model compounds. Figure 6-6 shows the effects of the vapor pressure on the aquasonolytic rate constants of the selected compounds under identical initial concentration.

Surprisingly, the aquasonolytic rate constants show an irregular variation with increasing vapor pressures. This demonstrates that the vapor pressure does not, or at least not directly affect aquasonolyses of the model compounds.

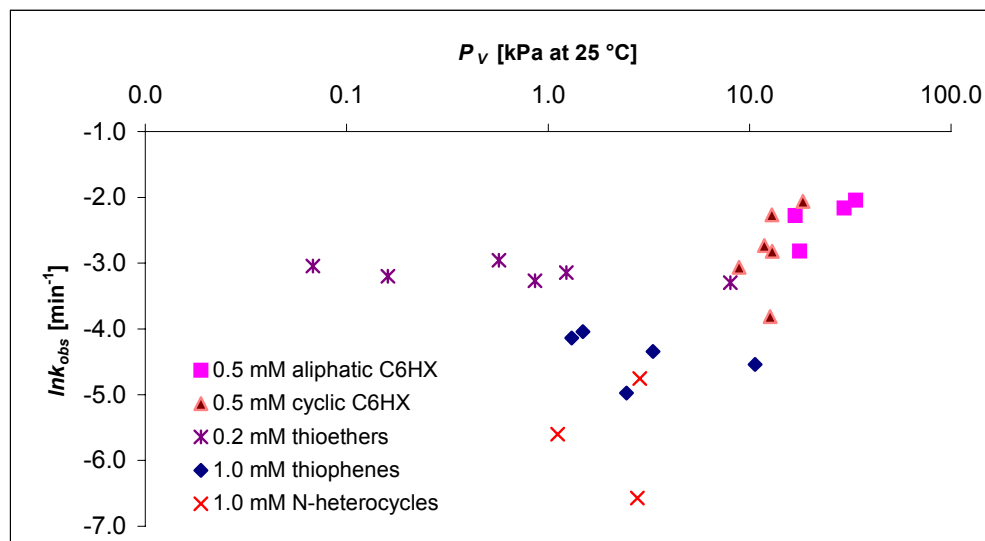


Figure 6-5 Effects of  $P_V$  of substrates from various substrate groups on  $k_{obs}$   
(500 mL, 850 kHz, 40 W, 295 K)

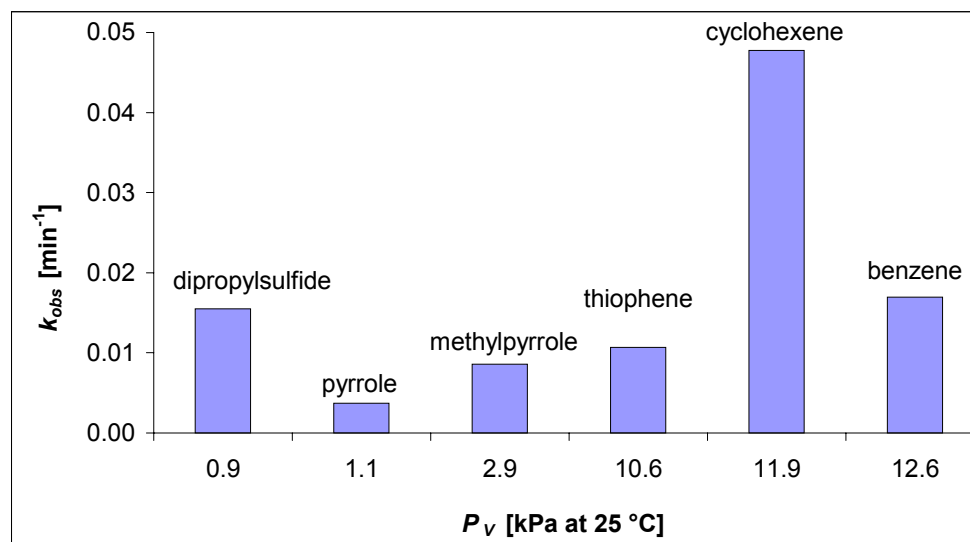


Figure 6-6 Effects of  $P_V$  of selected substrates on  $k_{obs}$  under identical ultrasonic conditions  
(1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

### 6.1.5 Roles of Hydrophobicity of Substrate on Aquasonolytic Rate Constants

Henglein et al. [34] observed that a higher hydrophobicity of substrates increases its capacity of trapping  $\cdot\text{OH}$  radicals. However, the vapor pressure of the scavenger (organic substrate) is not the determining factor. The effect was explained in terms of  $\cdot\text{OH}$  radical formation in gaseous bubbles, combination of  $\cdot\text{OH}$  radicals to form  $\text{H}_2\text{O}_2$  at the interfacial area, and enrichment of hydrophobic substrates in the bubbles, which undergo pyrolytic degradation [134].

#### 6.1.5.1 Effects of Octanol-Water Partition Coefficient of Substrate

The octanol-water partition coefficient ( $P_{OW}$ ) is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. It provides a thermodynamic measure of the tendency of the substance to prefer a nonaqueous or oily milieu rather than water (i.e. its hydrophilic/lipophilic balance). The octanol-water partition coefficient of a compound is defined as [184]:

$$P_{OW} = \frac{C_O}{C_w} \quad (E\ 6-2)$$

where  $P_{OW}$  is the octanol-water partition coefficient,  $C_O$  is the concentration of a chemical in octanol at equilibrium, and  $C_w$  is the concentration of a chemical in water at equilibrium.

In order to demonstrate the role of the hydrophobicity, the effect of octanol-water partition coefficients of organic substrates on aquasonolytic rate constants was investigated. Figure 6-7 shows the relationship of the aquasonolytic rate constants with the  $\text{Log}P_{OW}$  of the various model compounds. Figure 6-8 shows the relationship of the aquasonolytic rate constants with the  $\text{Log}P_{OW}$  of the selected model compounds under identical initial concentration.

Obviously, a higher  $\text{Log}P_{OW}$  results in a higher aquasonolytic rate constant, though few exceptional cases exist. To a certain extent, the volatility and/or the reactivity of organic substrates with intermediates (e.g., free radicals, atoms, and active molecules) generated in situ in bulk liquids, probably play a role. For example, the hydrophobicity of dipropyl sulfide is higher ( $\text{Log}P_{OW} = 2.88$  at 298 K), but its vapor pressure ( $P_V = 0.86$  kPa at 298 K) is very low. Thus it is sonicated very slowly.

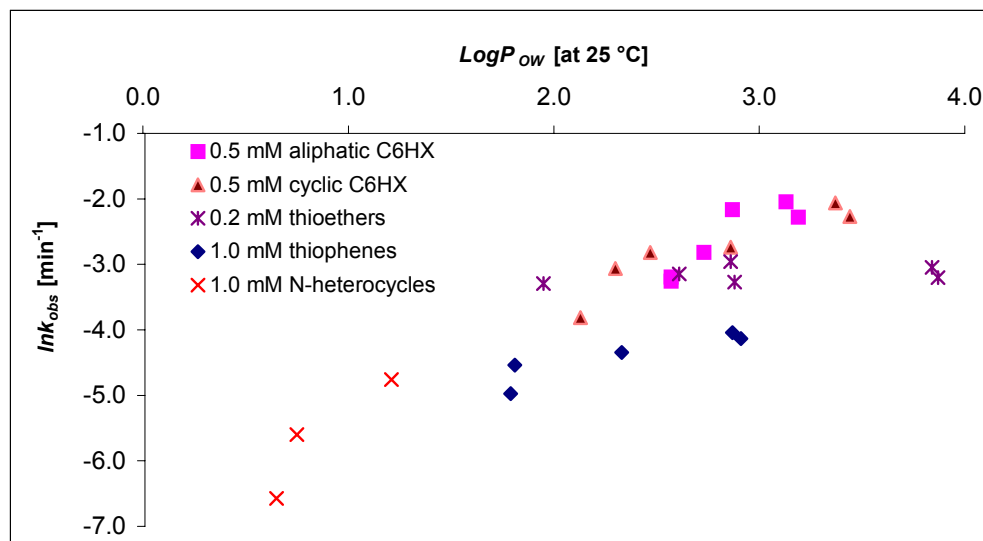


Figure 6-7 Effects of  $\text{Log}P_{OW}$  of substrates from various substrate groups on  $k_{obs}$  (500 mL, 850 kHz, 40 W, 295 K)

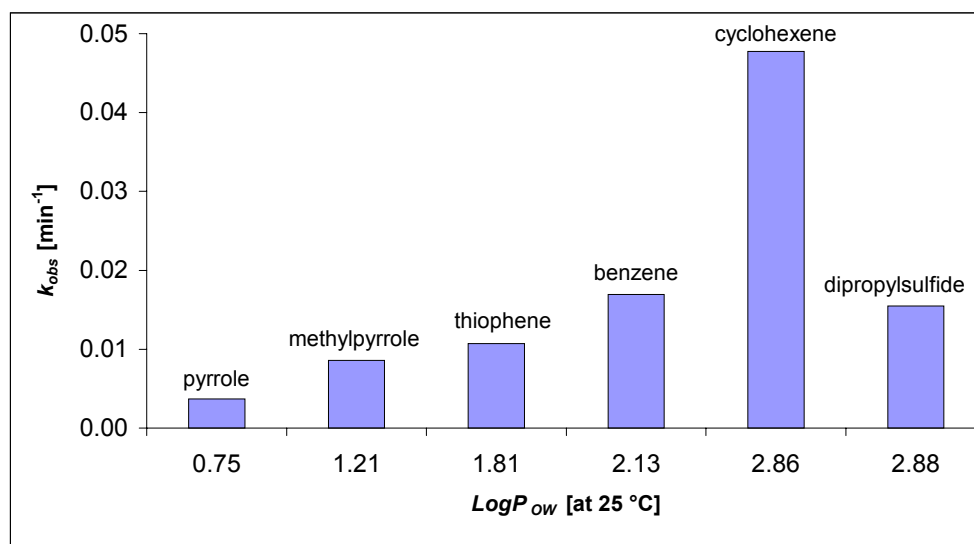


Figure 6-8 Effects of  $\text{Log}P_{OW}$  of selected substrates on  $k_{obs}$  under identical ultrasonic conditions (1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

### 6.1.5.2 Effects of Water Solubility

Since the water solubility ( $S_w$ ) among various compounds covers a wide range, it may more precisely reflect the dependence of the aquasonolysis on the hydrophobicity of the substrates than  $\text{Log}P_{OW}$ . Figure 6-9 shows the relationship between the aquasonolytic rate constant and the water solubility of various model compounds. Figure 6-10 shows the relationship between the



aqueous sonolytic rate constant and the water solubility of the selected model compounds under identical initial concentration. Indeed, a higher water solubility of the substrate results in a lower aqueous sonolytic rate constant.

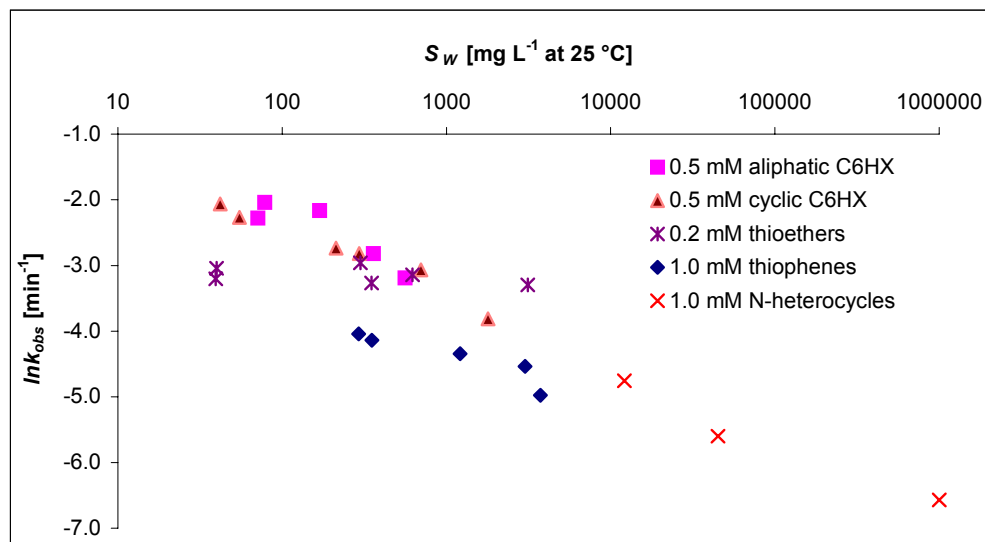


Figure 6-9 Effects of water solubility of substrates from various substrate groups on  $k_{obs}$  (500 mL, 850 kHz, 40 W, 295 K)

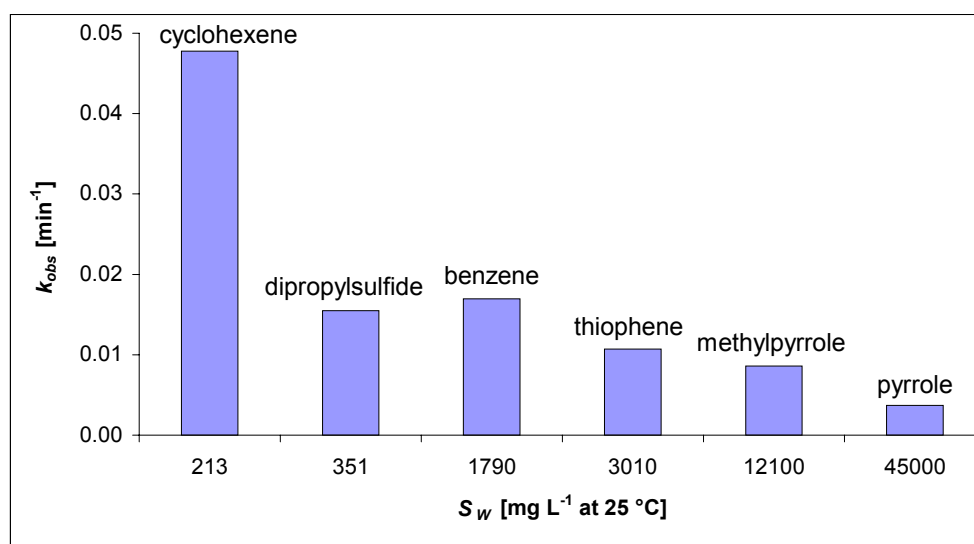


Figure 6-10 Effects of  $S_w$  of selected substrates on  $k_{obs}$  under identical ultrasonic conditions (1.0 mmol L<sup>-1</sup>, 500 mL, 850 kHz, 40 W, 295 K)

Based on Figure 6-9 and Figure 6-10, the water solubility has a profound influence when the water solubility is less than 1000 mg L<sup>-1</sup>. At the water solubility of over 10000 mg L<sup>-1</sup>, its effect is somewhat diminished. In order to demonstrate this dependence, the impact coefficients of water solubility ( $F_s$ ) were calculated as follows:

$$F_s = \frac{|k_{\max} - k_{\min}|}{|S_{W\max} - S_{W\min}|} \quad (E\ 6-3)$$

where  $k_{\max}$  is the maximum rate constant found for a range of water solubility, and  $S_{W\max}$  is the corresponding water solubility;  $k_{\min}$  is the minimal rate constant found for a range of water solubility, and  $S_{W\min}$  is the corresponding water solubility.

The calculation results are listed in Table 6-1.

*Table 6-1 Impact coefficients of  $S_w$  on aquasonolytic rate constants (Unit:  $L\ mg^{-1}\ min^{-1}$ )*

Range of $S_w$ ( $mg\ L^{-1}$ )	30 - 400	300 - 700	600 - 4000	> 10000
Cyclic $C_6H_x$	$2.68 \times 10^{-4}$	$3.19 \times 10^{-5}$	$2.26 \times 10^{-5}$	-
Aliphatic $C_6H_x$	$2.49 \times 10^{-4}$	$9.35 \times 10^{-5}$	-	-
Thiophenes	-	$2.67 \times 10^{-5}$	$2.4 \times 10^{-6}$	-
Sulfides	$4.29 \times 10^{-5}$	$1.85 \times 10^{-5}$	$2.39 \times 10^{-6}$	-
Disulfides	$1.65 \times 10^{-5}$	-	-	-
N-heterocycles	-	-	-	$6.07 \times 10^{-10}$

As a result, the water solubility does strongly influence the aquasonolytic rate of the model compounds in the range of 30 – 400  $mg\ L^{-1}$ . The effect decreases as the water solubility increases. When the water solubility is over 10000 (e.g. for pyrrole and pyridine), its effect is negligible. Hence the pyrolyses of hydrophilic organic compounds hardly occurs in this case, and aquasonolyses proceed very slowly.

This finding is consistent with previous studies [34, 134] and provides a complementary insight into the aquasonolytic mechanisms of organic substrates. This investigation demonstrates that hydrophobic volatile substrates are readily sonicated in aqueous solutions. Instead of the oxidation of the organic substrate by  $\cdot OH$  radicals and/or  $H_2O_2$ , the pyrolysis of the hydrophobic substrate in the collapsing bubbles and/or at the interfacial area dominates the sonolytic decomposition.

### 6.1.6 Effects of Initial Concentration of Organic Substrate on the Kinetics

In general, the aquasonolytic rate constants tend to decrease as the initial concentrations ( $C_0$ ) of substrates increases [35, 36, 96]. This effect is also observed in this investigation. The results are shown in Figure 6-11. Since the ratio of specific heats of the organic vapor is lower than that of air (Section 2.5.5), the organic compound entering the cavities might decrease the collapse temperature of the cavitation bubbles. More organic vapors in the cavities result in a lower collapse

temperature. It demonstrates indirectly that the pyrolysis of the organic substrate in the cavities is the predominant process for the aquasonolysis of the hydrophobic volatile substrate.

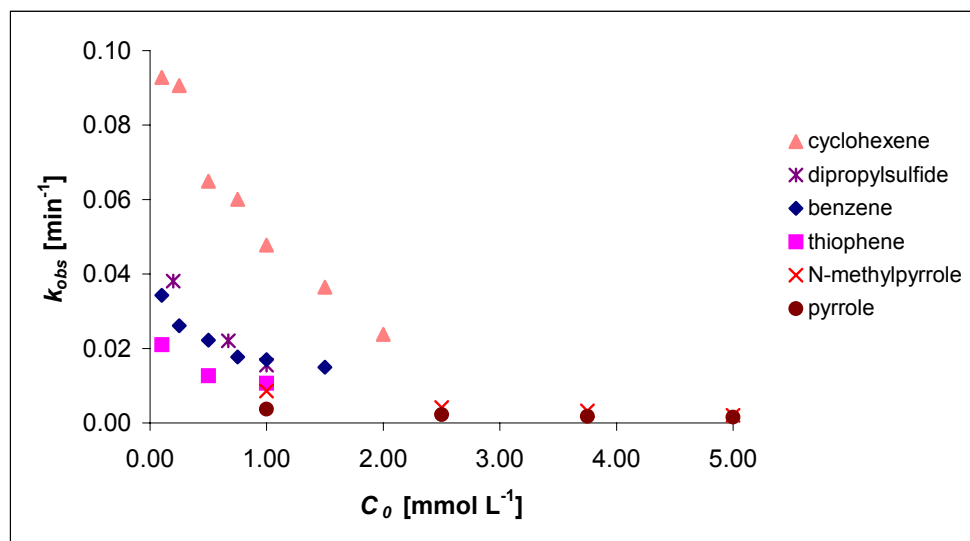


Figure 6-11 Effects of initial concentrations of substrates on  $k_{obs}$

(500 mL, 850 kHz, 40 W, 295 K)

Based on Figure 6-11, the effect of the initial concentrations of the substrates shows extreme difference among various compounds. The initial concentration influences the aquasonolysis of cyclohexene much more sharply than that of pyrrole. Probably, the hydrophobicity of organic substrates still plays an important role. In order to demonstrate this theory, the impact coefficients of the initial concentration ( $F_c$ ) are calculated as follows:

$$F_c = \frac{|k_{c_{max}} - k_{c_{min}}|}{|C_{max} - C_{min}|} \quad (E\ 6-4)$$

where  $k_{C_{max}}$  is the maximum rate constant of a compound, and  $C_{max}$  is the corresponding initial concentration;  $k_{C_{min}}$  is the minimal rate constant of a compound, and  $C_{min}$  is the corresponding initial concentration.

The results are listed in Figure 6-12. The water solubility indeed plays an essential role in the effect of initial concentrations of the model compounds. The effect decreases as the water solubility increases. This indicates that the pyrolysis of the hydrophobic organic compound in collapsing bubbles is the predominant pathway of its sonication, and the pyrolysis of the hydrophilic organic compound in collapsing bubbles hardly proceeds.

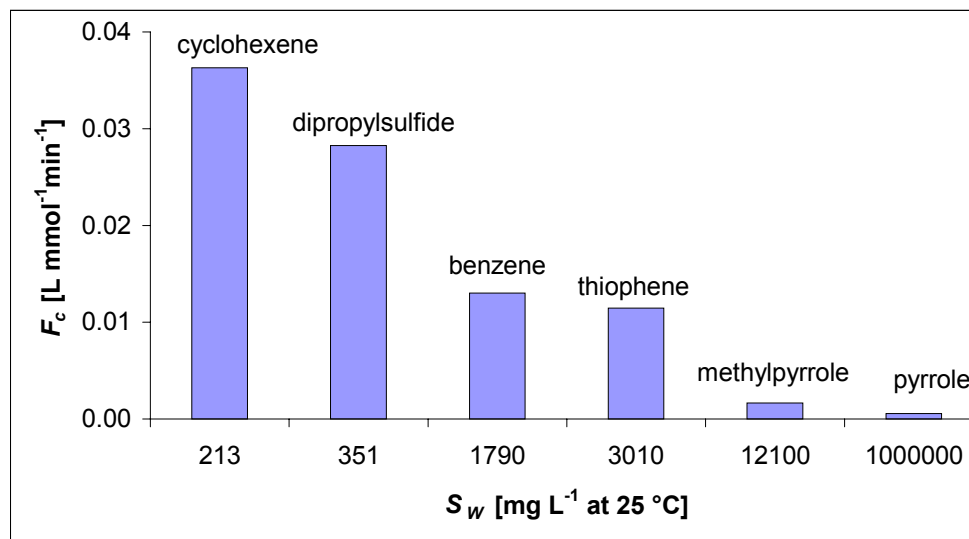


Figure 6-12 Impact coefficients of  $C_0$  of the selected compounds with various water solubility

## 6.2 Sonolyses of Organic Substrates

### 6.2.1 Effects of Volatility of Liquids on the Sonolytic Rates

DPPH is a well-known radical scavenger that scavenges any radicals produced in sonolysis. The scavenging reaction may proceed at the interface region or in the bulk solution. Thus, the rates of DPPH trapping in sonolysis can be used to show both the formation of free radicals and the potential for sonolyses of organic liquids.

A 60.0 mmol L<sup>-1</sup> DPPH solution was prepared by dissolving 139.0 mg DPPH (85%) in 5.0 mL methanol. 20 or 50  $\mu\text{L}$  of 60.0 mmol L<sup>-1</sup> DPPH solution was added into 3.0 mL pure organic liquid to detect the rate of DPPH consumption. Absorption spectra of DPPH in organic liquid were recorded with a Shimadzu UV-2102PC spectrophotometer ( $\lambda_{\text{max}} = 517 \text{ nm}$ ). The corresponding pure organic liquid was used as the blank solution.

#### 6.2.1.1 Rates of DPPH Trapping in Thiophenes

The rates of DPPH trapping in thiophene (TH), 2-methylthiophene (2MTH), 3-methylthiophene (3MTH), 2-ethylthiophene (ETH), and 2,5-dimethylthiophene (DMTH) at 208 and 283K were observed and compared as shown in Figure 6-13. Obviously, the rates of DPPH trapping in all thiophenes are much higher at 208 K than at 283 K. Furthermore, the substrate with the higher

boiling point shows a higher sonolytic rate at identical conditions of the ultrasonic irradiation. Thus, a low temperature and/or low vapor pressure of solvents increase the rates of DPPH trapping, and enhance sonolyses of thiophene and its derivatives as well.

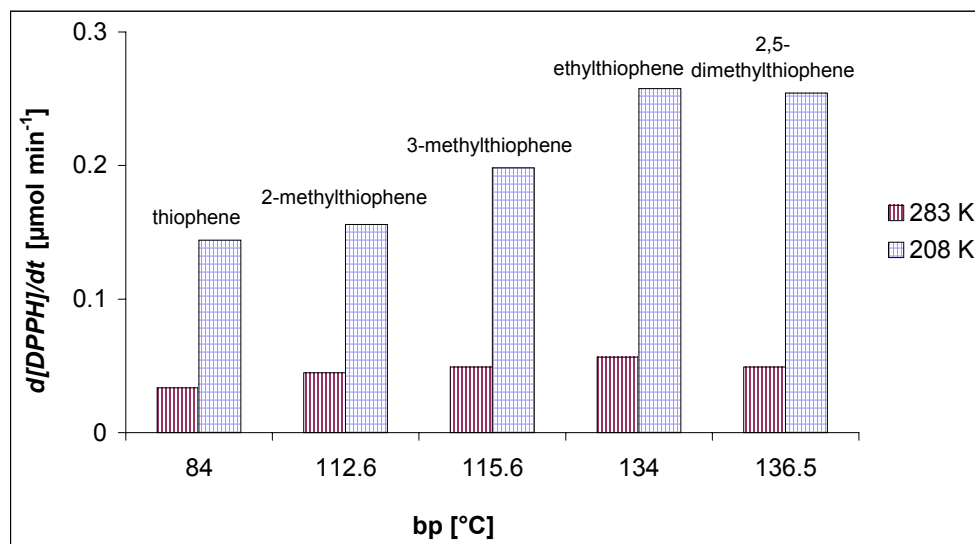


Figure 6-13 Rates of DPPH trapping in thiophenes at 208 K and 283 K  
(1.0 mmol L<sup>-1</sup> DPPH, 3.0 mL, 24 kHz, 30 W cm<sup>-2</sup>)

#### 6.2.1.2 Rates of DPPH Trapping in Thioethers

The rates of DPPH trapping in diethyl sulfide (DES), dibutyl sulfide (DBS), diethyl disulfide (DEDS), and dipropyl disulfide (DPDS) at 208 and 283K were observed and compared as shown in Figure 6-14.

Obviously, the rates of DPPH trapping are much higher at 208 K than at 283 K. Furthermore, the rates of DPPH trapping are higher in disulfides than in sulfides at both temperatures. Thus, the low temperature (i.e., low vapor pressure of solvents) increases the rates of DPPH trapping, and enhances sonolyses of thioethers as well.

In order to further proof the effect of vapor pressure of the solvent, the rates of DPPH trapping were investigated at different temperatures in dibutyl sulfide (DBS). Figure 6-15 shows the effect of vapor pressure on the rates of DPPH trapping in DBS. Vapor pressures are calculated using data from the NIST Webbook [155]. Indeed, the rates of DPPH trapping decrease as the vapor pressures of DBS increase.

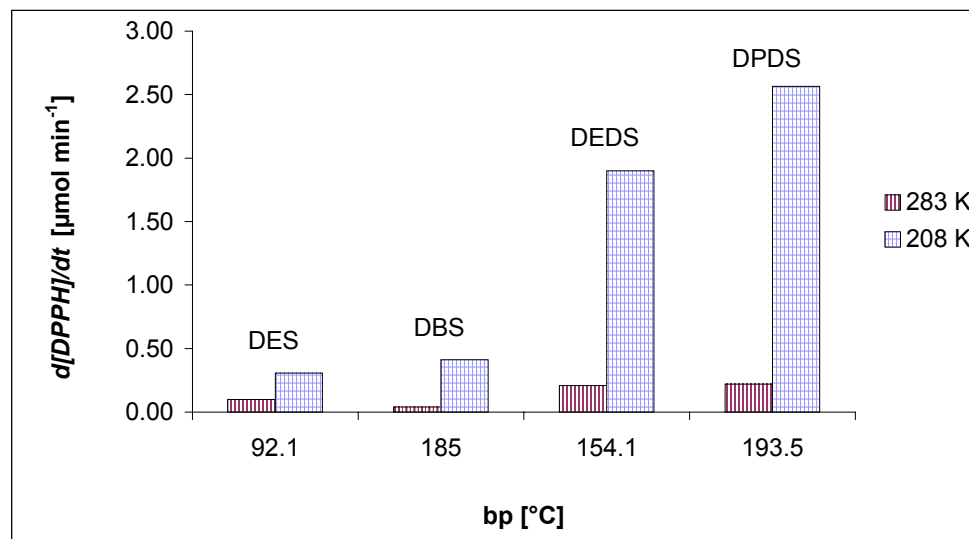


Figure 6-14 Rates of DPPH trapping in thioethers at 208 K and 283 K  
(1.0 mmol L<sup>-1</sup> DPPH, 3.0 mL, 24 kHz, 30 W cm<sup>-2</sup>)

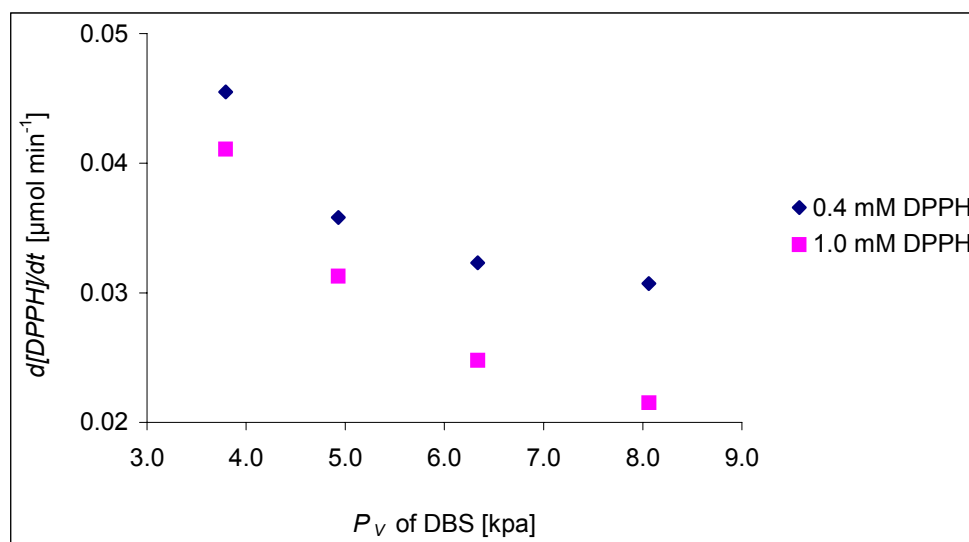


Figure 6-15 Effects of solvent vapor pressure on rate of DPPH trapping in DBS  
(3.0 mL, 24 kHz, 30 W cm<sup>-2</sup>)

In general, the maximum temperature reached inside a collapsing transient bubble may be taken to be inversely proportional to the solvent vapor pressure, and can be calculated using equation (E2-1):

$$T_{\max} = \frac{T_0 P_a (\gamma - 1)}{P_v} \quad (\text{E2-1})$$

where  $T_0$  is the liquid temperature,  $P_a$  is the acoustic pressure at initiation of collapse,  $\gamma$  is the ratio of specific heats, and  $P_v$  the vapor pressure of the solvent. For instance,  $P_v$  of DBS at 283 K is 3.8 kPa, and  $P_v$  of DBS at 298 K is 8.3 kPa.

If  $P_a^{283K} \approx P_a^{298K}$ ,

$$T_{\max}^{283k} / T_{\max}^{293k} = \frac{283 \times P_a^{283K} (\gamma - 1)}{3.8} \div \frac{298 \times P_a^{298K} (\gamma - 1)}{8.3} = 2.07 \quad (E\ 6-5)$$

This indicates that the maximum collapse temperature at 283 K is over twice as high as that at 298 K. The Arrhenius equation ( $k = Ae^{-E_a/RT_{\max}}$ ) was often employed to explain the reaction kinetics in the bubble as equation (E6-6):

$$\ln k = \ln A - \frac{E_a P_v}{RT_0 P_a (\gamma - 1)} \quad (E\ 6-6)$$

Hence, the reaction rate constant ( $k_{obs}$ ) decreases with increasing solvent vapor pressure ( $P_v$ ). The rates of DPPH trapping in thioethers are consistent with these assumptions.

## 6.2.2 Sonolyses of Selected C<sub>6</sub>H<sub>x</sub> Hydrocarbons at Low Temperature

### 6.2.2.1 Sonolyses of Aliphatic C<sub>6</sub>H<sub>x</sub> Hydrocarbons

Based on the gas chromatograms, not only products can be qualitatively found, but also the yield of products can be quantitatively measured. However, since some products (e.g., C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> species) are emitted into the air atmosphere, it is difficult to carry out an exact quantitative analysis. In addition, DPPH is immediately decolorized in hydrocarbon liquids with unsaturated bonds, and DPPH can not be used as scavenger to trap radicals generated in these hydrocarbon liquids. The pseudo-yield is used to describe their sonolytic potentials.

In general, the collapse temperature of cavitation bubbles in organic liquid is inversely proportional to its vapor pressure. Because of the lack of the data of vapor pressures of model substrates at low temperature, the boiling points instead of vapor pressures are used to correlate with the pseudo-yield (Section 5.1.2). The results are shown in Figure 6-16. Generally, the pseudo-yield increases as the boiling point increases, though some exceptional cases still exist.

Since organic vapors have the lower ratios of specific heat than water, the collapse intensity of cavities in organic liquids is weaker than in water, and the collapse temperature is much lower than in water [185, 186]. At relative low collapse temperature of cavitation bubbles, the thermostability of organic vapors can profoundly influence the sonolytic process. E.g., 1-hexyne has a much higher heat of formation (105.4 KJ mol<sup>-1</sup>) than 2,3-dimethyl-2-butene (-70.3 KJ mol<sup>-1</sup>), therefore, 2,3-dimethyl-2-butene is more thermostable than 1-hexyne, even though they have similar boiling points.

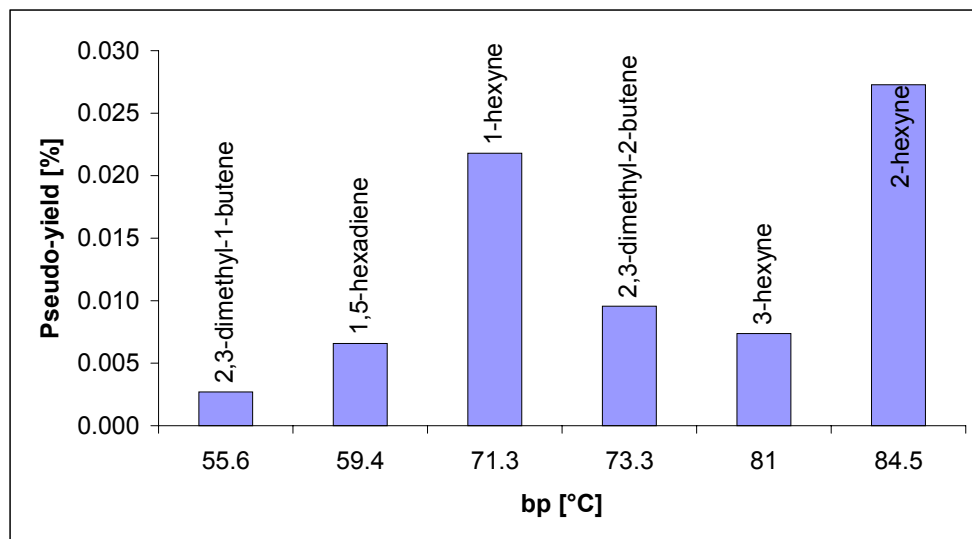


Figure 6-16 Sonolytic pseudo-yields versus boiling points of the selected aliphatic substrates

(24 kHz, 45 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h)

### 6.2.2.2 Cyclic C<sub>6</sub>H<sub>X</sub> Hydrocarbons

Table 5-3 shows pseudo-yields from sonolyses of cyclohexene and cyclohexadiene at low temperature. Pseudo-yields are ranked as being: 1,4-cyclohexadiene >> 1,3-cyclohexadiene >> cyclohexene.

Both 1,3-cyclohexadiene ( $\Delta_f H^\circ_{\text{gas}}=104.6 \text{ kJ mol}^{-1}$ ) and 1,4-cyclohexadiene ( $\Delta_f H^\circ_{\text{gas}}=104.8 \text{ kJ mol}^{-1}$ ) have similar heats of formation, but 1,4-cyclohexadiene ( $P_V = 8.88 \text{ kPa}$  at 298 K) has a higher boiling point or lower vapor pressure than 1,3-cyclohexadiene ( $P_V = 12.97 \text{ kPa}$  at 298 K). Hence, 1,4-cyclohexadiene is more readily sonolyzed than 1,3-cyclohexadiene. Furthermore, 1,3-cyclohexadiene has a much higher heat of formation than cyclohexene ( $\Delta_f H^\circ_{\text{gas}}=-4.32 \text{ kJ mol}^{-1}$ ,  $P_V = 11.87 \text{ kPa}$  at 298 K), indeed, 1,3-cyclohexadiene is more intensively sonolyzed than cyclohexene, even though they have similar boiling points and vapor pressures.

In conclusion, both the vapor pressure and the thermostability of organic substrate play an important role during the sonolysis of pure organic liquid.

### 6.2.3 Sonolytic Pseudo-Yields of the Selected N-Heterocycles

In order to evaluate the sonolytic difference among the N-heterocycles, the sonolytic pseudo-yields of pyrrole, N-methylpyrrole, and pyridine were investigated. The sonolytic pseudo-yields were calculated as equation (E5-1)



At normal temperature, no product was found during sonolyses of N-methylpyrrole and pyridine. Although a few products were found during the sonolysis of pyrrole at normal temperature, the pseudo-yield is over 18 times higher at low temperature (208 K) than at normal temperature (283 K). In addition, a higher boiling point results in a higher pseudo-yield. Figure 6-17 shows the results. This result is consistent with the results of sonolyses of the selected hydrocarbons and S-containing compounds (Section 6.2.1 and 6.2.2). This indicates again that the sonolytic rate of an organic liquid is inversely proportional to its vapor pressure.

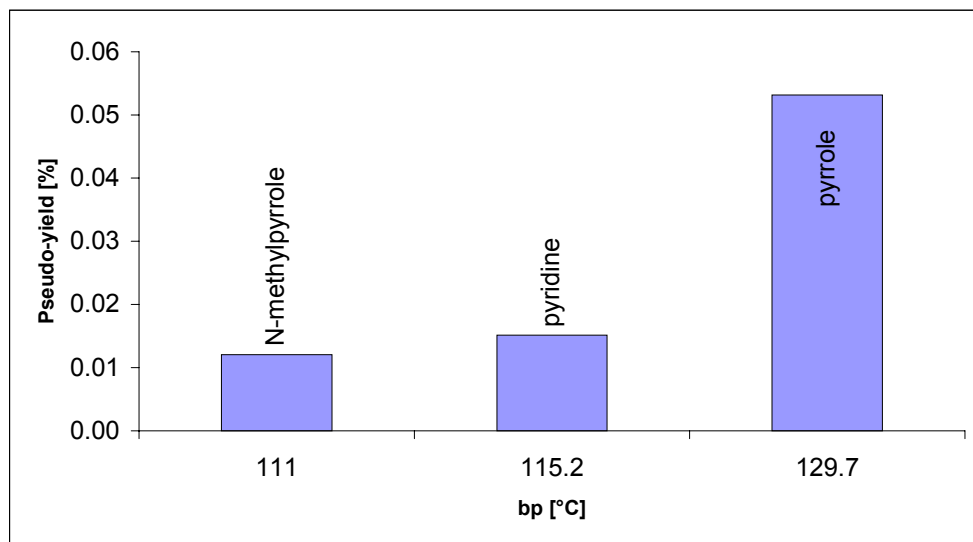


Figure 6-17 Sonolytic pseudo-yields versus boiling points of the selected N-heterocycles

(24 kHz, 30 W cm<sup>-2</sup>, 2.5 mL, 208 K, 4 h)

## 6.2.4 Effects of Ultrasonic Intensity and Density on Sonolyses of Organic Substrates

In general, increasing intensity will increase the sonochemical effects, since the collapse time, temperature, and pressure are dependent on the ultrasonic pressure amplitude. Bubble collapse will be more violent with higher intensity. However, the applied intensity or the acoustic amplitude also governs the maximum bubble size. With increasing pressure amplitude, the bubble may grow so large it will not collapse.

### 6.2.4.1 Effects of Ultrasonic Intensity and Density on the Formation of Benzene and 1,3-Cyclohexadiene from the Sonolysis of Cyclohexene

At low temperature, both the formation rates and yields of benzene and 1,3-cyclohexadiene from the sonolysis of cyclohexene, as shown in Figure 6-18 and Figure 6-19, increase with the rise of the ultrasonic intensity.

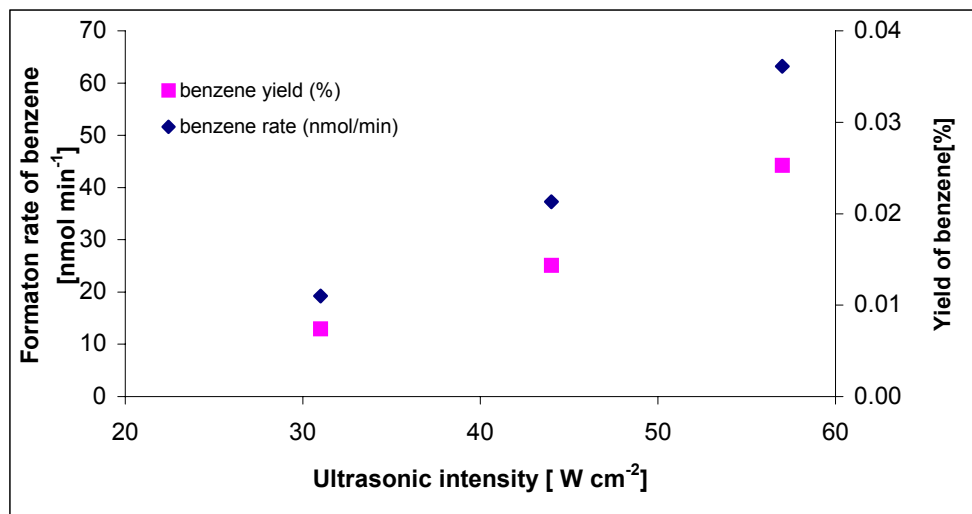


Figure 6-18 Formation rates of benzene vs. ultrasonic intensity in cyclohexene sonolysis (24 kHz, 2.5 mL, 208 K, 4 h)

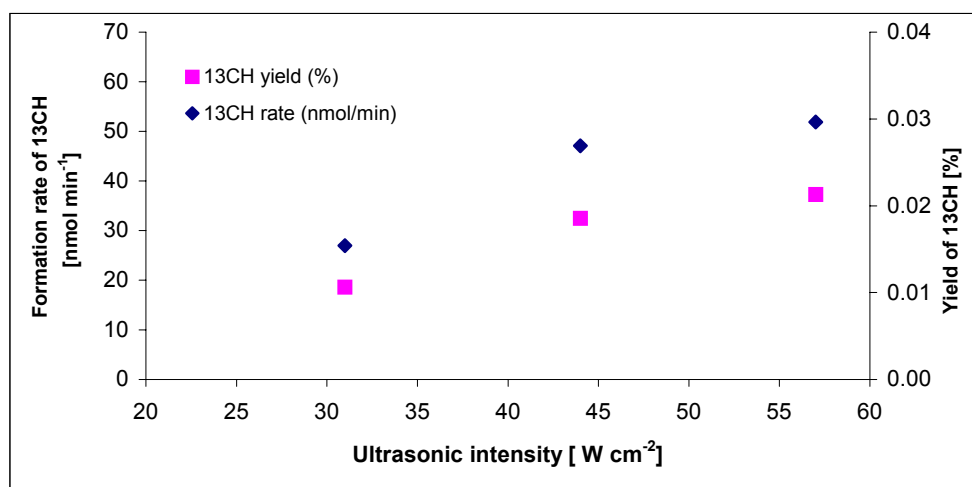


Figure 6-19 Effects of ultrasonic intensity on formation rates of 13CH from CE sonolysis (24 kHz, 2.5 mL, 208 K, 4 h, 13CH: 1,3-cyclohexadiene; CE: cyclohexene)

The ultrasonic density was regulated by changing the volume of the bulk liquid. Figure 6-20 and Figure 6-21 show the effects of the ultrasonic density. Based on Figure 6-20 and Figure 6-21, the formation rates of benzene and 1,3-cyclohexadiene obviously increase as the ultrasonic density increases. However, their yields do not regularly vary with the ultrasonic density.

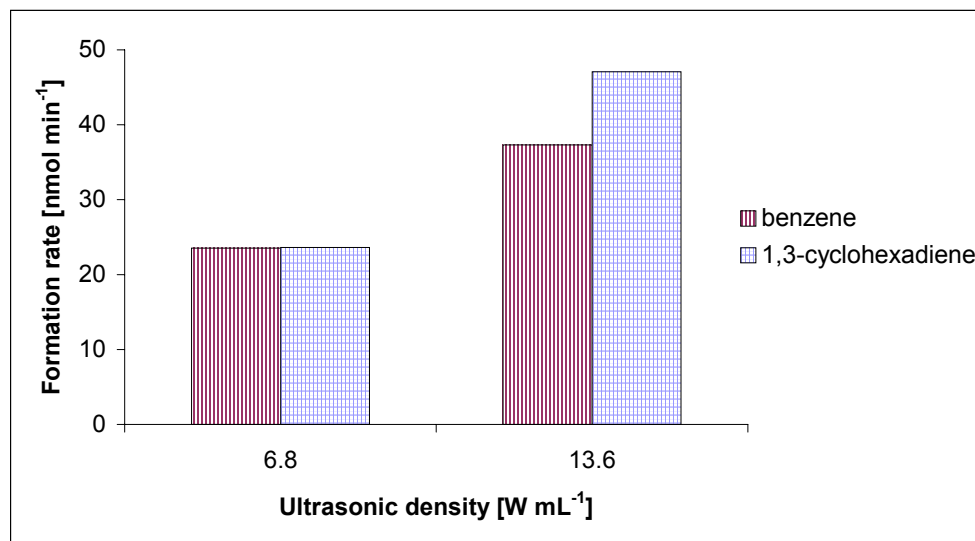


Figure 6-20 Formation rates of Ben and 13CH vs. ultrasonic density in the sonolysis of CE (24 kHz, 2.5 mL, 208 K, 4 h, Ben: benzene; 13CH: 1,3-cyclohexadiene; CE: cyclohexene)

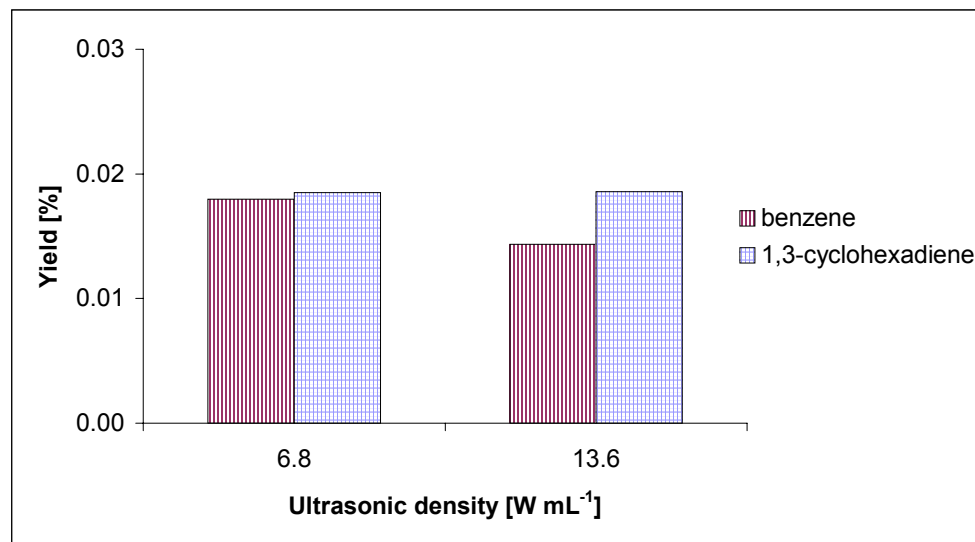


Figure 6-21 Effects of ultrasonic density on yields of Ben and 13CH in the sonolysis of CE (24 kHz, 2.5 mL, 208 K, 4 h, Ben: benzene; 13CH: 1,3-cyclohexadiene; CE: cyclohexene)

#### 6.2.4.2 Effects of Ultrasonic Intensity on Rates of DPPH Trapping

Figure 6-22 shows effects of ultrasonic intensity on the rates of DPPH trapping in dibutyl sulfide (DBS). According to Figure 6-22, increasing ultrasonic intensity increases the rates of DPPH trapping. Additionally, the effect of initial concentration of DPPH is negligible. This indicates that DPPH trapping takes place in the bulk liquid.

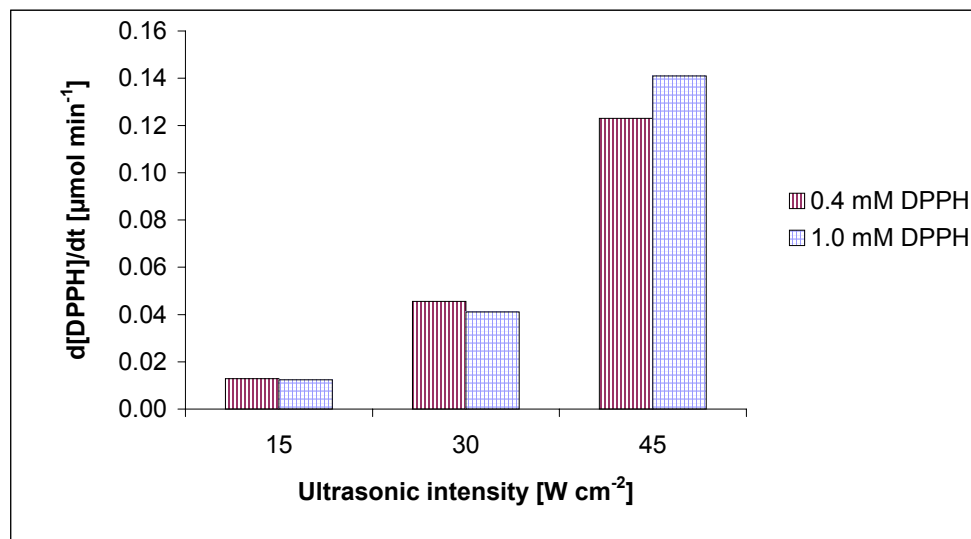


Figure 6-22 Effects of ultrasonic intensity on rates of DPPH trapping in DBS (3.0 mL, 24 kHz, 283 K)

### 6.3 Roles of Lipophobicity and Volatility of Hydrocarbons on Sonolyses in Nonaqueous Solutions

#### 6.3.1 Effects of $\text{Log}P_{OW}$ of Organic Solvents on Sonolyses of the Selected $\text{C}_6\text{H}_x$ Hydrocarbons

It has been reported that the hydrophobicity of organic solutes can affect the sonolysis in aqueous solutions [34, 134]. A lower water solubility of the organic solute results in faster aquasonolysis. Thus, the polarity relationship between the solvent and the volatile solute may affect sonolyses of the organic solutes in organic solvents.

The sonolytic rates of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, and cyclohexane in tetrachloroethylene (TCE), n-propanol, and n-decane were investigated. Sonolyses of the selected  $\text{C}_6\text{H}_x$  hydrocarbons followed pseudo-first-order kinetics. The dependence of the pseudo-first-order rate constants on  $\text{Log}P_{OW}$  of the model compounds are shown in Figure 6-23.

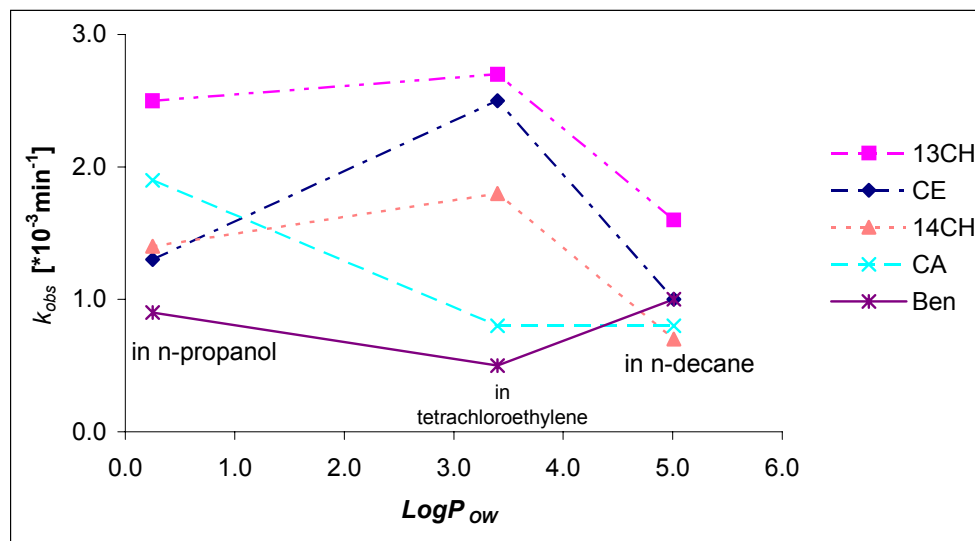


Figure 6-23 Effects of  $\text{Log}P_{OW}$  of solvents on the sonolytic rate constants  
(33.3 mmol L<sup>-1</sup> solution, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K)

(13CH: 1,3-cyclohexadiene; CE: cyclohexene; 14CH: 1,4-cyclohexadiene; CA: cyclohexane; Ben: benzene.)

In general, the rate constants are higher in polar solvents than in non-polar solvents. However, the rate constants of 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene in tetrachloroethylene are higher than those in n-propanol and n-decane. Obviously, the interaction of the substrates with chlorine (in situ generated from the sonolysis of tetrachloroethylene!) caused an increase in their sonolytic rates. Analyses of products proved this point (Section 5.2.2). In addition, due to its higher hydrophilicity, benzene is more rapidly decomposed in n-decane (non-polar solvent) than in n-propanol (polar solvent).

### 6.3.2 Effects of Vapor pressures of C<sub>6</sub>H<sub>x</sub> Hydrocarbons on Sonolytic Rates in Organic Solvents

The relationship between the pseudo-first-order rate constants and the vapor pressures of the selected solutes is shown in Figure 6-24.

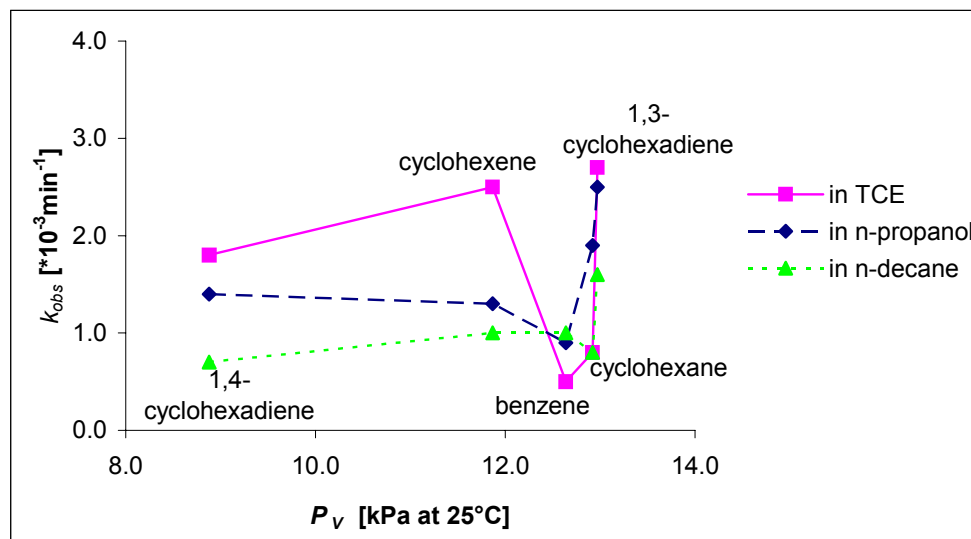


Figure 6-24 Effects of the vapor pressures of  $C_6$  substrates on  $k_{obs}$  in organic solvents (33.3 mmol L<sup>-1</sup> solution, 20 mL, 24 kHz, 45 W cm<sup>-2</sup>, 291 K, TCE: tetrachloroethylene)

In tetrachloroethylene, 1,3-cyclohexadiene is decomposed more rapidly than 1,4-cyclohexadiene, although they have similar heats of formation and reactivity with chlorine. In general, the sonolytic rate constants vary directly with the vapor pressure. However, the sonolysis of benzene is an exceptional case in n-propanol. N-propanol is a polar liquid ( $\text{Log}P_{OW} = 0.25$ ), and the hydrophilicity of benzene is the highest ( $\text{Log}P_{OW} = 2.13$ ) among the selected compounds. Therefore, benzene may hardly transfer from n-propanol bulk liquid into the cavitation bubbles.

Similarly, the sonolysis of cyclohexane is also an exceptional case in n-decane. N-decane is a non-polar solvent ( $\text{Log}P_{OW} = 5.01$ ), and the lipophilicity of cyclohexane is the highest ( $\text{Log}P_{OW} = 3.44$ ) among the selected compounds. Similarly, cyclohexane may hardly transfer from n-decane bulk liquid into the cavitation bubbles.

## 6.4 Sonochemical Mechanisms of Selected Organic Substrates

Sonolyses of  $C_6H_x$  hydrocarbons, thioethers, thiophenes, and N-heterocycles in aqueous solutions and nonaqueous liquids have been investigated. All investigations show that the thermal decomposition of the organic substrates in the collapsing cavitation bubbles is the predominant pathway of their sonochemistry. Based on the present experimental results and former studies on the pyrolytic mechanisms of the model compound, sonochemical mechanisms of the model

compounds are suggested as follows. Small products (< C<sub>4</sub> species) or products produced in the bulk liquid are not included.

### 6.4.1 Sonolyses of C<sub>6</sub>H<sub>X</sub> Hydrocarbons

All aliphatic C<sub>6</sub>H<sub>X</sub> hydrocarbons undergo unimolecular dissociation, then form the gaseous species, such as C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> hydrocarbons. Here the dehydrogenation mechanisms of sonolyses of the selected cyclic C<sub>6</sub>H<sub>X</sub> hydrocarbons are discussed, as shown in *F6-1 to F6-5*.

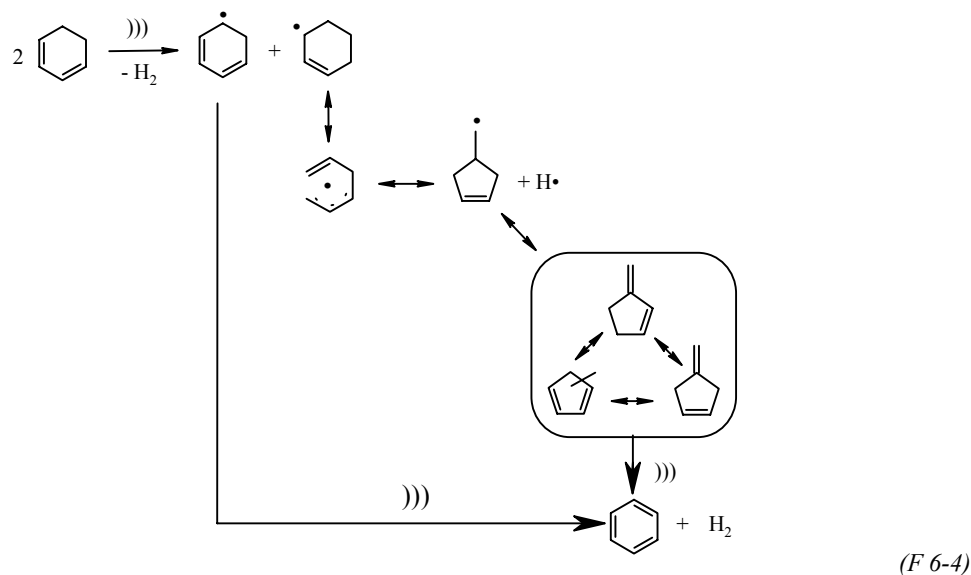
#### *Benzene sonolysis*



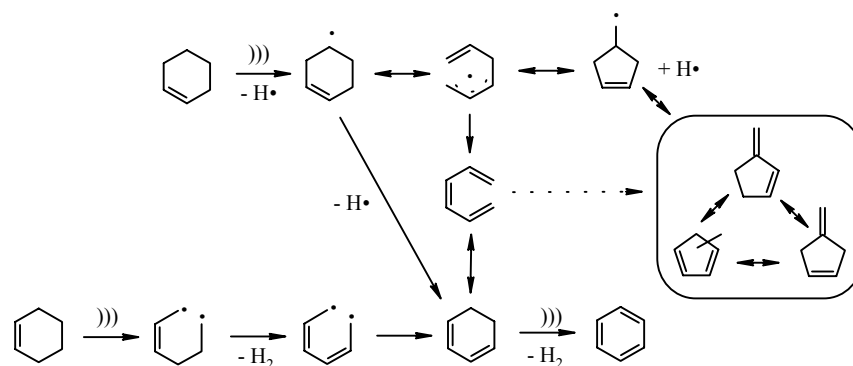
#### *1,4-Cyclohexadiene sonolysis*



#### *1,3-Cyclohexadiene sonolysis*



## Cyclohexene sonolysis

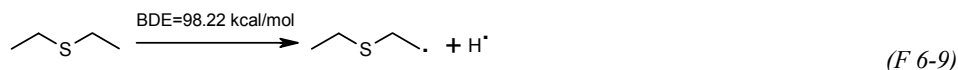
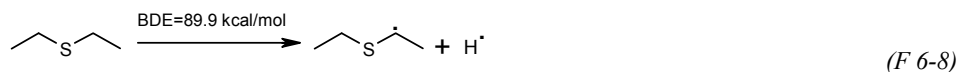
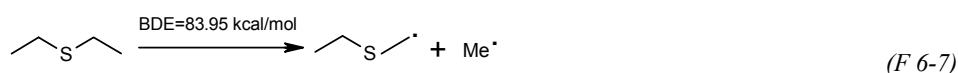


(F 6-5)

## 6.4.2 Sonolyses of Thioethers

*Unimolecular dissociation and combination of free radicals:*

According to the bond dissociation energies (BDEs), the bonds of C-S, S-S, or C-C of thioethers are orderly cracked under ultrasonic irradiation. Then the radicals are combined with each other. Montgomery et al. reported the BDEs of diethyl sulfide as following reactions (F6-6 to F6-9) [175], (1 kcal = 4.184 kJ).



The thermal decomposition of thioethers is a complex process, due to various BDEs within thioethers molecules. The cleavage of C-S bond in the collapsing bubbles is the predominant pathway of aquasonolyses of thioethers.

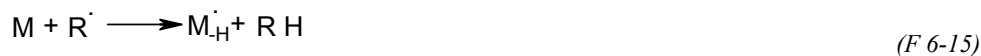
The formation of ethanethiol and methyl ethyl sulfide during the aquasonolysis of diethyl sulfide is regarded as a proof for the radical mechanism of the decomposition of diethyl sulfide. The formations of propanethiol and methyl propyl sulfide from the aquasonolysis of dipropyl sulfide, and the formations of allylthiol and methyl allyl sulfide from the aquasonolysis of diallyl sulfide



show the similar mechanism. Furthermore, the formation of propyl propenyl sulfide demonstrates the dehydrogenation of dipropyl sulfide during the aquasonolysis. RSH and RSR<sub>1</sub>H could then decompose to give alkyl, SH, RS, and R<sub>1</sub> radicals. Some of RS radicals might undergo further decomposition to give sulfur atoms and alkyl radicals.

However, due to the higher vapor pressure of DES (8.03 kPa at 298 K), no sulfurized product, thiol, thiophene, and dehydrogenated products can be detected from the sonolysis of pure diethyl sulfide even at low temperature; only little CS<sub>2</sub>, and SO<sub>2</sub> are detected at low temperature. Due to lower vapor pressure, diallyl sulfide (1.23 kPa at 298 K), dipropyl sulfide (0.86 kPa at 298 K), dibutyl sulfide (0.16 kPa at 298 K), diethyl disulfide (0.57 kPa at 298 K), and dipropyl disulfide (0.068 kPa at 298 K) can undergo the cleavage of C-S, S-S, and C-C bonds, and even the cleavage of C-H bonds at 283 K.

The formation of disulfides, thiols, smaller sulfides, and hydrocarbons during sonolyses of thioethers can be most readily explained by the following reactions (F6-10 – F6-15):



In addition, the combination of free radicals can readily produce disulfide and hydrocarbon species, such as diallyl disulfide and 1,5-hexadiene from the sonolysis of diallyl sulfide. (Reaction F6-16 to F6-18):

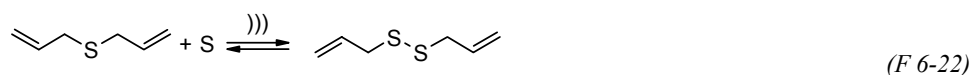


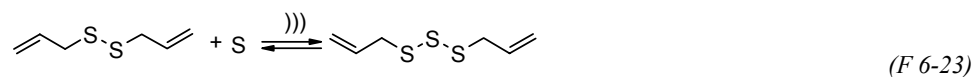
Similarly, disulfides additionally undergo the dissociation of the S-S bond. This demonstrates a radical mechanism forming ethanethiol, diethyl sulfide, methyl ethyl disulfide, ethyl propyl disulfide, and ethyl butyl disulfide from the aquasonolysis of diethyl disulfide. Furthermore, diethyl sulfide, methyl ethyl sulfide, methyl ethyl disulfide, dimethyl disulfide, and diethyl trisulfide are formed during the sonolysis of diethyl disulfide (Reaction *F6-19 to F6-21*).



#### *Sulfuration:*

Diethyl sulfide appeared to be completely inert toward sulfuration with  $\text{S}_8$  in  $\text{Me}_2\text{SO}-d_6$ , even when heated at ca. 353-363 K for several days. Under the same conditions, diallyl sulfide is partially converted to diallyl disulfide [187]. In addition, S atoms react with  $\text{CH}_3\text{SCH}_3$  to generate elemental sulfur and  $\text{CH}_3\text{SSCH}_3$  as major primary products [188]. Under ultrasonic irradiation, S atoms may be released from sonolyses of thioethers. Hence, it is possible that  $\text{S}_8$  is formed by combination of S atoms. Both S atoms and  $\text{S}_8$  may readily react with diallyl sulfide in bulk liquid under ultrasonic irradiation. These reactions result in faster sonication of diallyl sulfide in aqueous solutions. Similarly, trisulfide would also be produced by sulfuration of disulfide (reaction *F6-22 to F-6-23*):



*Cyclization:*

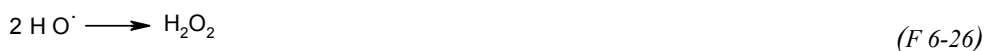
It is proposed that some RS or RSR<sub>1</sub> radicals might undergo further decomposition to give biradical intermediates during their aquasonolyses. The various biradicals rearrange to sulfur-containing rings. Rings containing multiple sulfur atoms are produced by sulfuration of sulfur-containing rings [188].

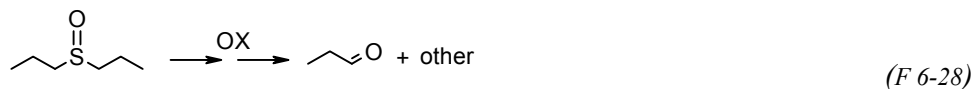
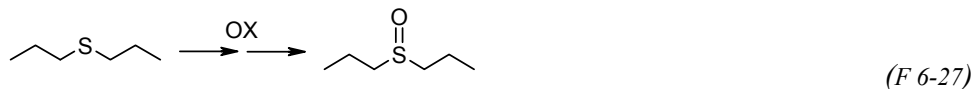


However, the formation of dimethylthiophene from the aquasonolysis of diallyl sulfide is regarded as proof for a complex reaction system.

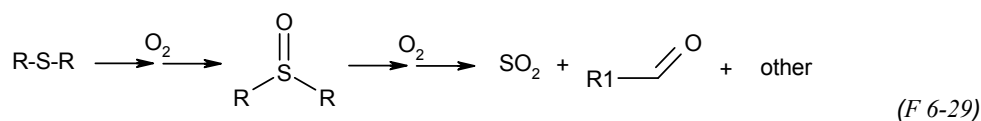
*Oxidation:*

Many of the properties of sulfides stem from the fact that divalent sulfur is a reducing agent; it is easily oxidized to higher oxidation states. Treatment of a sulfide with 1.0 mol of 30 % aqueous H<sub>2</sub>O<sub>2</sub> at room temperature gives a sulfoxide as illustrated during the oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide [174]. Spurlock and Reifsneider found dibutyl sulfoxide is the principal product of the aquasonolysis of dibutyl sulfide. Butyl sulfonic acid, dibutyl sulfone, butyric acid, and carbon monoxide are the minor products [26]. During aquasonolyses of thioethers, COS was found to be the common oxidized product. In addition, propanal and dipropyl sulfoxide were detected during the aquasonolysis of dipropyl sulfide. Propanal was detected during the aquasonolysis of diallyl sulfide. Since the principal products from the ultrasonic irradiation of water are H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>, and various data support the hypothesis of the intermediary of hydroxyl radicals and hydrogen atoms [7], the sonochemical mechanisms of oxidation of sulfides in aqueous solutions are proposed as following reactions:





During sonolyses of pure thioethers,  $\text{SO}_2$  and aldehydes were found in the atmosphere of air. Diethyl sulfoxide is obtained during the sonolysis of diethyl disulfide. The oxidation pathways are proposed as reaction (F6-29).



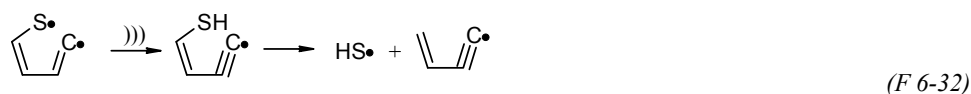
In addition, thiols are also oxidized to disulfides by molecular oxygen [174]:

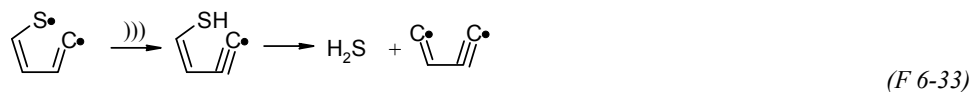


### 6.4.3 Sonolyses of Thiophenes

The ultrasonic cleavage of the thiophene ring is the principal sonochemical mechanism of thiophene. It has been concluded that the pyrolysis of thiophene is initiated by C-S bond fission to form the  $\text{C}_4\text{H}_4\text{S}$  biradical which reacts to give  $\text{C}_4\text{H}_3 + \text{SH}$  together with the reaction giving  $\text{C}_3\text{H}_4 + \text{CS}$  [167].

*Cleavage of C-S bond and formation of biradical:*



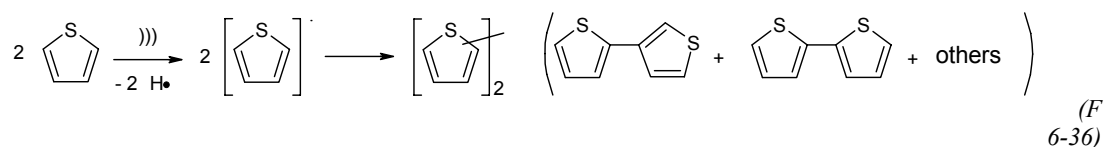


$\text{C}_4\text{H}_3$  radical is further decomposed and dehydrogenated to form solid carbon, hydrogen, and unsaturated hydrocarbons.  $\text{C}_4\text{H}_4\text{S}$  biradical is further decomposed to give CS and  $\text{C}_3\text{H}_4$ .  $\text{CS}_2$  is formed by CS reaction. Other pathways of  $\text{CS}_2$  formation should further be investigated.



*Dimerization:*

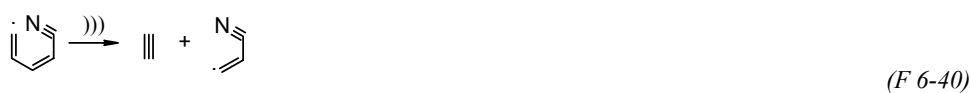
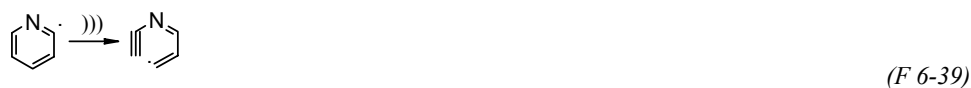
Dimers are also the common products from sonolyses of thiophenes. Obviously, the fission of C-H bonds of thiophenes also occurs under ultrasonic irradiation.  $\text{C}_4\text{H}_3\text{S}$  radical will then participate in polymerization as follow:



## 6.4.4 Sonolyses of N-Heterocycles

### 6.4.4.1 Sonolysis of Pyridine

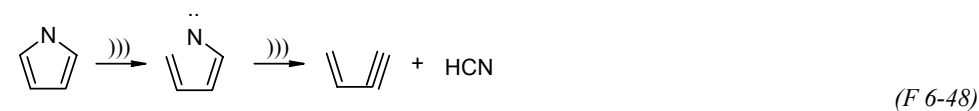
Earlier studies clearly demonstrated the radical chain nature of the thermal decomposition. Some studies in fact proposed that the pyrolysis is initiated primarily via C-H fission, most likely from the carbon atom adjacent to the nitrogen atom [180, 189]. The o-pyridyl radical is believed to be the most stable of the three possible pyridyls and the only major pyridyl radical whose fission leads to the primary decomposition products, HCN,  $\text{C}_2\text{H}_2$ , and HCCCN. Based on the mechanism of the pyrolysis of pyridine, the sonolytic mechanism of pyridine is postulated to be as follows:



#### 6.4.4.2 Sonolysis of Pyrrole

Lifshitz et al. and Mackie et al. have reported the comprehensive studies of the pyrolysis of pyrrole [178, 190, 191]. The major products of pyrrole pyrolysis are cis-crotonitrile ( $\text{CH}_3\text{CHCHCN}$ ), HCN,  $\text{C}_3\text{H}_4$  (propyne and allene), and allyl cyanide ( $\text{CH}_2\text{CHCH}_2\text{CN}$ ). These products are formed via a common open-chain biradical intermediate. Based on the pyrolytic mechanism of pyrrole proposed by Lifshitz et al. [178], the sonolytic mechanism of pyrrole is suggested as follows:





#### 6.4.4.3 Sonolysis of *N*-Methylpyrrole

There are three different modes of initiation in *N*-methylpyrrole pyrolysis [177]: the removal of the methyl group from the ring to give methyl and pyrrole radicals, the direct unimolecular cleavage of the pyrrole ring, and isomerization reactions of *N*-methylpyrrole.

The product pyrrole clearly indicates that the ejection of the methyl group from the ring is an important initiation step.



Other small species are commonly formed via the cleavage of the pyrrole ring. Since the thermal rearrangement of *N*-methylpyrrole to 2-methylpyrrole and pyridine had been reported in earlier studies [176, 177], the thermal rearrangement of *N*-methylpyrrole should further be investigated in the sonolysis of *N*-methylpyrrole by improving GC analytic methods in the future.

## 7 Conclusions

### 7.1 Sonolysis in Aqueous Solutions

#### 7.1.1 Aquasonolytic Products

C-C bonds fission takes place during aquasonolyses of the selected aliphatic hydrocarbons, cyclohexane, and 1-methylcyclopentane. In addition, the high concentrations of benzene are formed during aquasonolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene. This shows that the dehydrogenation of the  $C_6H_X$  ring occurs. Meanwhile, many volatile products from radical reactions and oxidation are found during aquasonolyses of the selected cyclic  $C_6H_X$  hydrocarbons.

$CS_2$ , COS, thiols, thiirane, lower sulfides, butenyne, and butadiene are found as major very volatile products during aquasonolyses of the selected thioethers. This indicates that C-S bonds fission in thioethers occurred by ultrasonic irradiation. Thiophene, benzene, 1,5-hexadiene, and cyclopentadiene are also obtained during the aquasonolysis of diallyl sulfide by a network of free radical reactions. Furthermore, trisulfides, trithiolane, and other cyclic thiolanes as volatile products are detected.

$CS_2$ ,  $C_4H_4$ ,  $C_4H_2$ , and COS are the most commonly occurring very volatile products, and dimers are the major volatile products during aquasonolyses of the selected thiophenes.

Because of very high water solubility, the aquasonolytic rates of pyrrole and pyridine are very slow. No product is found from the aquasonolysis of  $5 \text{ mmol L}^{-1}$  pyridine in 6 h, only little HCC-CN and benzene are found from the aquasonolysis of  $5 \text{ mmol L}^{-1}$  pyrrole in 6 h. However, more products from the aquasonolysis of N-methylpyrrole are identified due to the lower water solubility and higher aquasonolytic rate. HCCCN and  $H_2C=CHCN$  are the most common nitrogen-containing products of the aquasonolysis of N-methylpyrrole.  $C_4H_4$  and  $C_4H_X$  are the major hydrocarbon products. In addition, benzene is observed during the aquasonolysis of N-methylpyrrole.

In conclusion, products stem from pyrolyses of organic substrates during the collapse of cavitation bubbles, as long as the organic substrates transfer into the cavitation bubbles. It appears that the pyrolysis in hot spots is the dominant degradation pathway of aquasonolyses of the volatile



substrates with higher hydrophobicity. Along with the increase in the hydrophilicity of volatile organic substrates, pyrolyses are remarkably diminished.

### 7.1.2 Aquasonolytic Kinetics

The aquasonolytic rates of cyclic and aliphatic  $C_6H_x$ , thiophenes, thioethers, and N-heterocyclic compounds strictly follow pseudo-first-order kinetics. Their aquasonolytic rate constants show over a 90-fold variation at constant acoustic power intensity, frequency, and temperature.

Higher Henry's Law constants result in higher aquasonolytic rates of the model compounds, but the aquasonolytic rate constant does not directly vary with vapor pressure and the thermostability. In contrast, the water solubility and  $LogP_{OW}$  strongly affect the aquasonolytic rate. A higher hydrophobicity results in higher aquasonolytic rate. Moreover, the aquasonolytic rate constants decrease with a rise of the initial concentrations of the substrates.

Hence, the transfer of the volatile organic substrate between the bulk liquid and the cavitation bubbles is essential for the aquasonolysis. Although the volatility of the organic substrates is a basic factor for the transfer, it is not a determining factor. Indeed, the hydrophobicity of the volatile substrate dominates the transfer and the aquasonolysis.

In addition, the reactivity of organic substrates with the active intermediates, such as radicals, atoms, and molecules in situ generated in the aquasonolysis, profoundly affects the sonochemical reaction.

## 7.2 Sonolysis in Nonaqueous Solutions

The sonolytic rates of benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, and cyclohexane in tetrachloroethylene, n-propanol, and n-decane were observed. Sonolyses of selected  $C_6H_x$  substrates in organic solvents follow pseudo-first-order kinetics.

A higher vapor pressure of the volatile solutes results in a higher pseudo-first-order rate constant. Generally, the cyclic hydrocarbons are sonoconverted more rapidly in polar than in non-polar solvents. As aquasonolysis, the polarity relationship between the substrate and the solvent also affects the transfer from the bulk liquid into the cavitation bubbles, as well as sonolytic rates and the yields of products.

Benzene is generated through cavitation pyrolyses of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene in n-decane, n-propanol, and tetrachloroethylene. Surprisingly, a higher sonolytic

rate resulted in a higher yield of benzene. It can be concluded that  $C_6H_X$  substrates are sonoconverted in the presence of investigated solvents in disagreement with pericyclic reactions. The overall reaction of these sonolyses is preceded via a complex radical network.

The sonoconversion in tetrachloroethylene is accompanied by the formation of some chlorinated products. Chlorinated products such as chlorobenzene are detected during the sonolysis of benzene in tetrachloroethylene under the catalysis of  $FeCl_3$ .

## 7.3 Sonolyses of Pure Organic Liquids

### 7.3.1 Sonolytic Products

Due to their higher vapor pressures, sonolyses of pure  $C_6H_X$  hydrocarbons do not occur at normal temperature. At low temperature, some small molecules are formed during sonolyses of the selected aliphatic  $C_6H_X$  hydrocarbons. There,  $C_3H_X$ ,  $C_4H_X$ , and  $C_5H_X$  products generated from the cleavage of C-C bonds are most common. Furthermore,  $C_6H_X$  products from radical recombination can also be observed. However, larger species (over  $C_6$ ) can not be found.

Similarly, some small molecules are also formed during sonolyses of the selected cyclic  $C_6H_X$  hydrocarbons at low temperature. There, the  $C_3H_X$ ,  $C_4H_X$ , and  $C_5H_X$  products generated from the cleavage of C-C bonds are most common. Especially, products such as benzene are generated by the dehydrogenation and  $C_6$  molecular rearrangement of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene.

No product is found from sonolyses of thiophenes at normal temperature. However, at low temperature,  $CS_2$ , dimer, and thiophene formed by cleavage of alkyls are the most common sulfur-containing products.  $C_4H_2$ ,  $C_4H_4$ ,  $C_5H_4$ ,  $C_5H_6$ , and  $C_6H_6$  are the common hydrocarbons. Also, some oxidized products are detected, e.g.,  $SO_2$ , COS, furan, and aldehydes.

Sulfurized products,  $CS_2$ , lower sulfides, and thiophene are the most common sulfur-containing products from sonolyses of the selected thioethers. Some hydrocarbons are detected during sonolyses of disulfides. More hydrocarbons are observed during the sonolysis of diallyl sulfide, such as 1,5-hexadiene, 1,3-cyclohexadiene, and benzene. Furthermore, some oxidized products can be also detected, e.g.,  $SO_2$  and aldehydes.

Small molecules are formed during sonolyses of the selected N-heterocycles at low temperature. There, 2-propenenitrile ( $H_2C=CHCN$ ) and 1-buten-3-yne ( $C_4H_4$ ) generated from the cleavage of C-C and C-N bonds are most common. In addition, pyrrole and furan are formed during the sonolysis

of N-methylpyrrole,  $C_5H_x$  and  $C_6H_x$  species are formed during sonolyses of pyridine and pyrrole. Furthermore, products from radical recombination are also observed, such as cyanogen (CNCN) from pyridine, and cyanoacetylene (HCCCN) from pyrrole.

All of these products demonstrate that the model compounds undergo pyrolyses and complex radical reactions during the ultrasonic irradiation at low temperature.

### 7.3.2 Role of Volatility of Organic Liquids on the Sonolysis

DPPH has been successfully used to probe the sonolytic potential of thioethers and thiophenes. The rates of DPPH trapping are strongly dependent on the liquid temperature. The rates of DPPH trapping in thioethers and thiophenes are much higher at 208 than at 283 K. Furthermore, substrates with the higher boiling points show higher sonolytic rates at identical conditions of the ultrasonic irradiation. Indeed, it is higher in disulfides than in sulfides at identical temperatures. Thus, the low temperature (i.e., low vapor pressure) enhances sonolyses of thioethers and thiophenes.

In general, the sonolytic yield increases as the boiling points of organic substrates increase. During sonolyses of the selected thioethers, the low temperature also increases the yields of low sulfides, thiols,  $CS_2$ , and oxidized products as well. Furthermore, the low temperature also causes the formations of  $SO_2$  and thiophene. This demonstrates the enhancement effect of low temperature on sonolyses of organic liquids.

Sonolyses of  $C_6H_x$  hydrocarbons and N-heterocycles are also influenced by the temperature and vapor pressure of the organic liquids. Little sonochemical reaction occurs in  $C_6H_x$  hydrocarbons and N-heterocycles at normal temperature, but many sonochemical reactions are observed at low temperature. The sonolytic pseudo-yield of pyrrole is over 18 fold higher at 208 K than at 283 K.

In addition, the thermostability of organic vapors and ultrasonic intensity also profoundly influence the sonolytic behavior of pure organic liquid.

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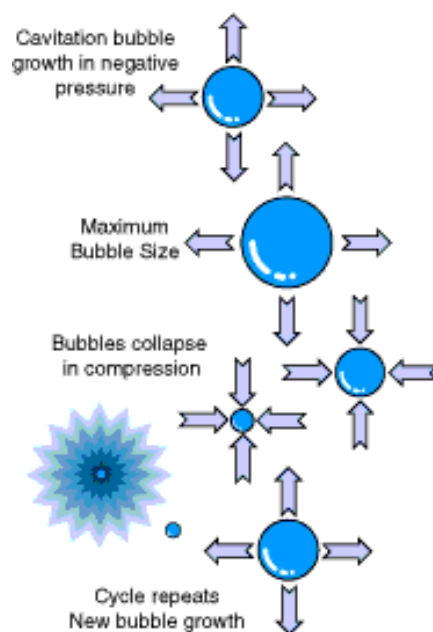
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### 9.3 Pictures of Sonochemistry



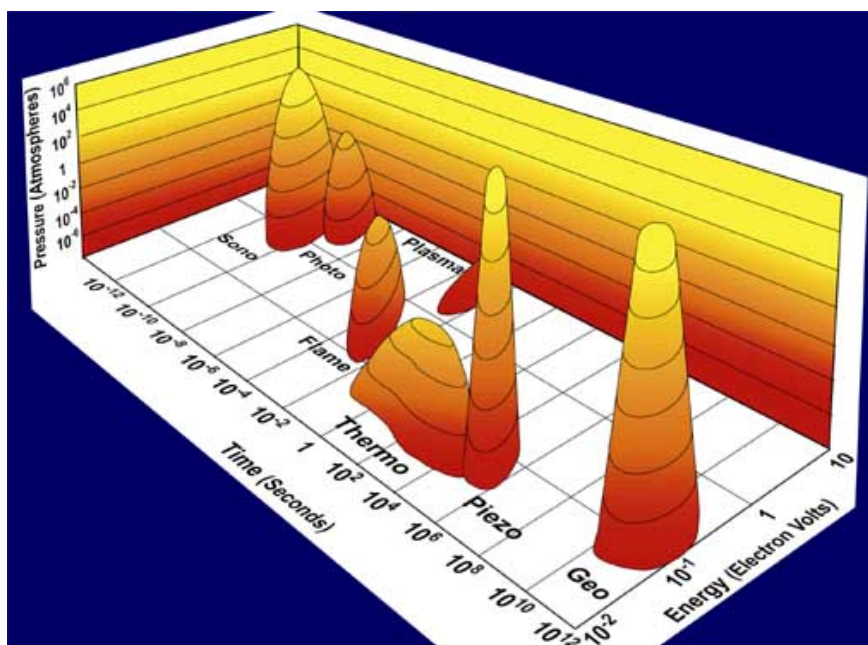
Picture 1 **Sonochemistry:** Sound waves can create high-energy bubbles in liquids. Intense heat and quick cooling of these bubbles speed up chemical reactions.  
[[www.aip.org/success/soundinvestment/](http://www.aip.org/success/soundinvestment/)]



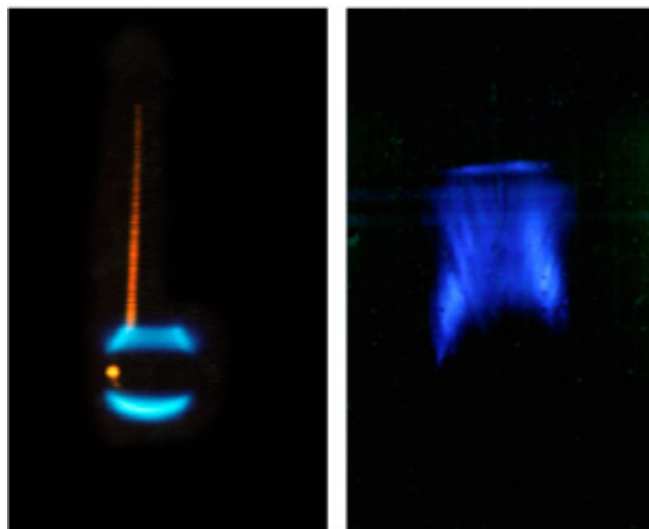
Picture 2 **Cavitation and Implosion:** Cavitation bubbles are created at sites of rarefaction as the liquid fractures or tears because of the negative pressure of the sound wave in the liquid.  
[[www.variclean.nl/theory.html](http://www.variclean.nl/theory.html)]



Picture 3 **Cavitation bubbles:** When a gas bubble in a liquid is excited by ultrasonic acoustic waves, it can emit short flashes of light suggestive of extreme temperatures inside the bubble. (Cover photo credit: K. S. Suslick and K. J. Kolbeck, *Nature*, 25 July 2002) [<http://www.scs.uiuc.edu/suslick/execsummsono.html>]



Picture 4 Sonochemistry in relationship to other forms of chemistry (Photo credit: K. S. Suslick, *Scientific American*, Feb. 1989) [[www.scs.uiuc.edu/suslick/execsummsono.html](http://www.scs.uiuc.edu/suslick/execsummsono.html)]



*Picture 5* **Sonoluminescence:** The left frame is a picture of a 4-millimeter titanium sphere (Mentor Corp) oscillating at 27 kHz in water. Xenon gas was dissolved into the liquid to enhance the light emission (blue) from the cavitation bubbles near the surface of the metal. On the right is a picture of sonoluminescence generated at 1 MHz. Note that in this case the bubbles oscillate and emit light in the "bulk" of water, far from the source of sound. (Photo credit: Carlos G Camara)

[[www.acoustics.org/press/140th/camara.htm](http://www.acoustics.org/press/140th/camara.htm)]



*Picture 6* **Ultrasonic Cleaning Devices (Simple Sonoreactor):** Ultrasound generates or grows bubbles in water. Ultrasonic cleaning is also dependent on the cavitation bubbles.

[[www.cb-chemie.de:8888/cbWeb/products?group=8](http://www.cb-chemie.de:8888/cbWeb/products?group=8)]

### Milestones of Sonochemistry

1867	Early observations of cavitation (TOMLINSON, GERNEZ)
1880	Discovery of the piezoelectric effect
1883	Earliest ultrasonic transducer by GALTON
1894	Cavitation as phenomenon recognized and investigated on propeller blades of HMS Daring (THORNYCROFT and BARVABY, Minutes of Proceedings of the Institution of Civil Engineers 122 (1895) 51)
1915-17	Pioneering work on ultrasonic acoustics by LANGEVIN
1917	First mathematical model for cavitation collapse predicting enormous local temperatures and pressures (RAYLEIGH)
1927	First paper on chemical effects of ultrasound published (RICHARDS and LOOMIS, J. Am. Chem. Soc. 49 (1927) 3086)
1933-35	Observation of sonoluminescence effects
1933	Reports on the reduction in the viscosity of polymer solutions by ultrasound
1943	First patent on cleaning by ultrasound (German Pat. 733.470)
1944	First patent on emulsification by ultrasound (Swiss Pat. 394.390)
1950s	Intensification of cavitation and ultrasound research, increasing number of applications using ultrasound
1950	Effect of ultrasound on chemical reactions involving metals (RENAUD, Bull. Soc. Chim. Fr. (1950) 1044)
1950	Hot spot model (NOLTINGK and NEPPIRAS)
1953	First review on the effects of ultrasound (BARNARTT, Quart. Rev. 7 (1953) 84)
1963	Introduction of plastic ultrasonic welding
1964	First monograph on physical, chemical and biological effects of ultrasound (ELPINER)
1970s	Renaissance of sonochemistry research
since 1980	Growing research on sonochemical effects
1986	First ever international meeting on sonochemistry
1990	Foundation of the European Society of Sonochemistry and ESS 1 Meeting

Picture 7 **Milestones of Sonochemistry:** European Society of Sonochemistry, [\[http://www.fb-chemie.uni-rostock.de/ess/intro.htm\]](http://www.fb-chemie.uni-rostock.de/ess/intro.htm)

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	For M. S. degree:	Synthesis of Long-chain Alkylaniline Based on the Idea of Clean Production.	
	For B. S. degree:	Synthesis of Methylmetsulfuron.	

Jena, 2005-03-10

Zhi-Lin Wu

## **Selbständigkeitserklärung**

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen Angefertigt habe.

Jena, 2005-03-10

Zhi-Lin Wu

Ort, Datum

Unterschrift des Verfassers