

## Roles of Hydrophobicity and Volatility of Organic Substrates on Sonolytic Kinetics in Aqueous Solutions

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The aquasonolytic rate constants of cyclic  $C_6H_x$ , aliphatic  $C_6H_x$ , thioethers, thiophenes, and N-heterocyclic compounds show over a 90-fold variation under identical conditions of ultrasonic irradiations. Henry's Law constant of the substrate has a substantial effect on the aquasonolytic rate; a higher Henry's Law constant leads to a higher aquasonolytic rate constant, which indicates the transfer process of organic substrate between bulk liquid and cavitation bubbles is essential for aquasonolysis. The aquasonolytic rate constants, however, dramatically show an irregular variation with increasing vapor pressure among various substrates. Although the volatility of substrate has been widely regarded as a basic factor influencing aquasonolysis, it seems that vapor pressure of substrate is not a determining one that accounts for the difference of aquasonolytic rate constants. In contrast, the hydrophobic parameters of volatile substrate such as water solubility and octanol–water partition coefficient have shown obvious correlation with the aquasonolytic rate constant for the model compounds; a higher hydrophobicity of volatile substrate results in a higher aquasonolytic rate constant. It could be concluded that the transfer process from bulk liquid to cavitation bubbles and the aquasonolytic kinetics of organic substrate are jointly controlled by the hydrophobicity and volatility; therein the hydrophobicity dominates the transfer process and the aquasonolysis of volatile substrate.

### Introduction

High-intensity ultrasound traveling through water generates small cavitation bubbles that enlarge and implode, creating tremendous temperature (5000 K) and pressure (1000 atm).<sup>1–5</sup> In such an unusual chemical environment, water undergoes thermal decomposition to release atomic and radical species ( $\cdot H$ ,  $\cdot OH$ ).<sup>6–8</sup> These active species can recombine to form hydrogen and hydrogen peroxide or attack an organic substrate. Furthermore, volatile organic compound in cavitation bubbles or nearby can also participate in the primary sonochemical reactions and is pyrolyzed during sonication.<sup>9–12</sup>

Generally, the sonochemical degradation of organic compound is strongly dependent on the bulk liquid temperature and the nature of dissolved gas, because the reaction temperature inside collapsing bubbles is inversely proportional to the vapor pressure of solvent, and directly proportional to the ratio of specific heats ( $\gamma = C_p/C_v$ ) of dissolved gas.<sup>13–18</sup> Since the ratios of specific heats of volatile organic solutes are lower than those of air, increasing organic vapors in cavitation bubbles would attenuate the collapsing intensity, the collapsing temperature, and the sonochemical reaction.<sup>19–22</sup> As a matter of fact, low concentrations of hydrocarbons, short-chain aliphatic alcohols, and organic acids and bases suppress sonoluminescence in water.<sup>23–28</sup> The intensity of emitted light decreases with increasing concentrations of alcohols, and the extent of quenching increases as the length of the alkyl chains of alcohols increases.

Earlier investigators have stated a few influences of nature of substrates on kinetics and mechanisms of sonolytic destructions of organic chemicals.<sup>9,29–32</sup> Weissler et al. investigated

the effect of the amount of  $CCl_4$  (0.01–10 mL) on the sonolytic yield of iodine in 20 mL of KI solution in 1950.<sup>9</sup> They found that 0.01 mL of  $CCl_4$  is optimum and that larger amounts of  $CCl_4$  cause excessive scattering of the ultrasonic energy and therefore lower yields. Reifsnieder et al. demonstrated that the relative proportions of products ( $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_2$ , and  $C_2H_6$ ) depend 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.<sup>29</sup>

One important contribution comes from Henglein and co-workers, who have shown that the efficiency of  $\cdot OH$  radical scavenging is correlated to the hydrophobicity of solutes during aqueous sonolyses.<sup>30</sup> Increasing hydrophobicity increases the capacity of solute for trapping  $\cdot OH$  radicals. However, the vapor pressure of scavenger (organic solute) is not a determining factor. Effects are explained in terms of  $\cdot OH$  radical formation in gaseous bubbles, combination of  $\cdot OH$  radicals to form  $H_2O_2$  at the interfacial area, and enrichment of hydrophobic solutes in the bubbles.

Henry's Law constant might be strongly associated with the solute transfer rate from bulk liquid to cavitation bubbles during the sonochemical destruction of organic chemicals;<sup>33,34</sup> as it were, increasing vapor pressure results in more solutes diffusing into the bubbles and undergoing pyrolytic decomposition as the bubbles collapse.<sup>35,36</sup> Since both the hydrophobicity and vapor pressure of organic substrate are correlated to the Henry's Law constants of substrates, there is a need to understand how exactly these two factors influence the sonolysis of organic substrates in aqueous solutions.

The objective of this paper is to demonstrate the effects of Henry's Law constants, vapor pressures, octanol–water partition coefficients, as well as water solubility of substrates on the

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**TABLE 1: Properties of Model Compounds and Their Aquasonolytic Rate Constants**

compound groups	no.	name	CAS	$S_w$ (mg L <sup>-1</sup> )	$\log P_{ow}$	$P_v$ (kPa)	$K_H$ (kPa L mol <sup>-1</sup> )	purity (%)	$k_{obs}$ (min <sup>-1</sup> )	$R^2$
cyclic C <sub>6</sub> H <sub>x</sub>	1	benzene	71-43-2	1790	2.13	12.6 4	562.4	99.7	0.02 21	0.99 5
	2	1,4-cyclohexadiene	628-41-1	700	2.3	8.88	10537.8	98	0.04 67	0.99 3
	3	1,3-cyclohexadiene	592-57-4	295	2.47	12.9 7	8551.8	97	0.05 96	0.98 9
	4	cyclohexene	110-83-8	213	2.86	11.8 7	4610.3	99.5	0.06 49	0.99 5
	5	cyclohexane	110-82-7	55	3.44	12.9 2	15198.8	99	0.10 36	1.00 0
	6	methylcyclopentane	96-37-7	42	3.37	18.4 0	36781.0	97	0.12 73	0.99 8
aliphatic C <sub>6</sub> H <sub>x</sub>	1	2-hexyne	764-35-2		2.57			98	0.03 85	0.98 1
	2	3-hexyne	928-49-4	559	2.57			98	0.04 12	0.98 4
	3	1-hexyne	693-02-7	360	2.73	17.7 3	4042.9	97	0.05 98	0.99 1
	4	2,3-dimethyl-2-butene	563-7 9-1	71	3.19	16.8 0	59781.8	97	0.10 26	0.99 5
	5	1,5-hexadiene	592-42-7	169	2.87	29.4 6	14286.8	97	0.11 51	0.99 6
	6	2,3-dimethyl-1-butene	563-78-0	78.5	3.13	33.6 0	42860.5	99	0.12 98	0.99 7
thiophenes	1	tetrahydrothiophene	110-01-0	3730	1.79	2.45	61.9	97	0.00 69	0.99 3
	2	thiophene	110-02-1	3010	1.81	10.6 3	295.9	98	0.01 07	0.98 8
	3	2-methylthiophene	554-14-3	1210	2.33	3.32	327.3	97	0.01 30	0.99 4
	4	2,5-dimethylthiophene	638-02-8	352	2.91	1.31	361.7	98	0.01 60	0.99 3
	5	2-ethylthiophene	872-55-9	292	2.87	1.49	434.7	97	0.01 76	0.99 8
thioethers	1	diethyl sulfide	352-93-2	3130	1.95	8.03	90.3	98	0.03 71	0.99 8
	2	dipropyl sulfide	111-47-7	351	2.88	0.86	247.2	97	0.03 81	1.00 0
	3	dibutyl sulfide	544-40-1	39.4	3.87	0.16	435.7	98	0.04 07	0.99 7
	4	diallyl sulfide	592-88-1	621	2.61	1.23	136.8	95	0.04 31	0.99 3
	5	dipropyl disulfide	629-19-6	39.9	3.84	0.07	382.0	97	0.04 76	0.99 8
	6	diethyl disulfide	110-81-6	300	2.86	0.57	217.8	99	0.05 19	0.99 7
N-heterocycles	1	pyridine	110-86-1	1000000	0.65	2.77	1.1	99.8	0.00 14	0.98 3
	2	pyrrole	109-97-7	45000	0.75	1.11	1.8	97	0.00 37	0.99 6
	3	N-methylpyrrole	96-54-8	12100	1.21	2.85	19.7	98	0.00 86	0.98 3

sonolytic kinetics of cyclic C<sub>6</sub>H<sub>x</sub>, aliphatic C<sub>6</sub>H<sub>x</sub>, thioethers, thiophenes, and N-heterocyclic compounds in aqueous solutions and to elucidate the dominant factor that controls the aquasonolysis (sonolysis in aqueous solutions) of volatile substrate.

## Experimental Section

**Materials and Reagents.** All chemicals were used as received from Fluka and Sigma-Aldrich. Table 1 shows their physicochemical parameters and purities. Physicochemical parameters were adopted from SRC PhysProp Database.<sup>37</sup>

**Ultrasonic Device and Irradiation Conditions.** The device consists of an ultrasound generator, an ultrasound transducer, and a double-walled cylindrical glass reactor (Meinhardt Ultraschalltechnik, Leipzig). The structure of applied apparatus for ultrasonic irradiation is shown in Figure 1. The technological parameters of the ultrasonic device have been described elsewhere.<sup>38,39</sup> The ultrasonic transducer operated continuously at 850 kHz under air atmosphere. The electrical power output was 120 W. The applied ultrasonic power determined through calorimetric measurement was 40 W, and the acoustic intensity was 2 W cm<sup>-2</sup>. The temperature of bulk liquid inside the reactor was maintained at 22 °C by 10 °C circulating cooling water. Chemicals were diluted to a given concentration using purified water.

Two parallel aliquots (5 + 5 mL) of the sonicated solution were periodically extracted from the reactor by airtight syringes, analyzed by headspace/gas chromatography (GC), and returned to the reactor after analysis. The irradiation volume was kept constant at 500 mL. The averages of parallel data were calculated to analyze the aquasonolytic rate constants. Moreover, all sonication experiments were conducted twice in parallel. The errors of all parallel data were under 5%. The averages of parallel aquasonolytic rate constants were calculated and taken into account in analyses of sonochemical kinetics.

**GC Analyses.** Quantitative analyses of the model compounds were performed by headspace/GC/flame ionization detection (FID). Headspace conditions: DANI HSS 86.50, equilibration time 20 min at 70 °C. GC conditions: HP5890 series II/FID, carrier gas H<sub>2</sub>. HP-5 capillary column: 30 m × 0.32 mm ×

0.25 μm. GC column head pressures were kept at 3 or 5 psi, and GC oven temperatures were kept constant between 35 and 100 °C depending on the nature of various chemicals. GC analysis time is 5 min per sample.

## Results and Discussion

**Comparison of Aquasonolytic Rate Constants of Model Compounds.** Pseudo-first-order kinetics has been widely employed in mechanistic studies.<sup>40</sup> The integrated rate equation (F1) for pseudo-first-order kinetics is generally applied for the investigation of aquasonolytic rates when a limited number of data points are available

$$\ln \frac{C_t}{C_0} = -k_{obs}t \quad \text{or} \quad \frac{C_t}{C_0} = e^{-k_{obs}t} \quad (\text{F1})$$

where  $C_0$  is the initial concentration of substrate,  $C_t$  is its concentration at later times,  $t$  is the ultrasonic irradiation time, and  $k_{obs}$  is the pseudo-first-order rate constant (aquasonolytic rate constant).

The aquasonolytic rate constants and the correlation coefficients ( $R^2$  values) determined for the studied substrates are shown in Table 1. The  $R^2$  values shown in Table 1 indicate that the aquasonolyses of all model compounds strictly follow pseudo-first-order kinetics. Figure 2 is a column figure for aquasonolytic rate constants of various model compounds. As shown in Figure 2, a wide range of aquasonolytic rate constants is observed for these investigated compounds under the same sonication conditions. Of these aquasonolytic rate constants, 2,3-dimethyl-1-butene shows the highest value, which is about 90-fold higher than the lowest value for pyridine. To explain the variation of kinetics, the dependences on the relevant physicochemical properties of the model compounds were studied.

**Effect of Henry's Law Constant on Aquasonolytic Rate Constant.** Henry's Law constant ( $K_H$ ) characterizes the relative amount of a substrate that will enter the vapor bubbles; hence this parameter has been investigated to identify its dependence on sonolysis. Henry's Law constant is strongly associated with

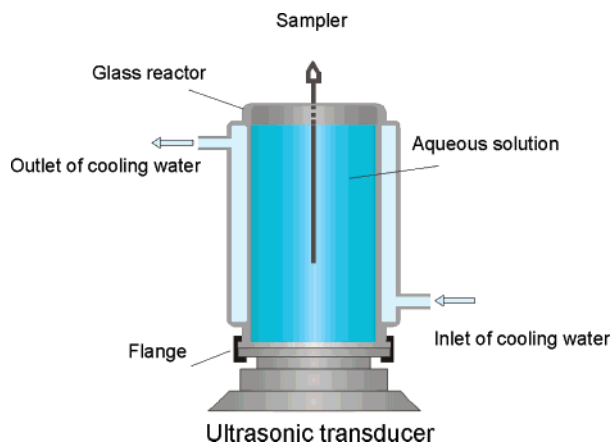


Figure 1. Scheme of the applied apparatus for ultrasonic irradiation.

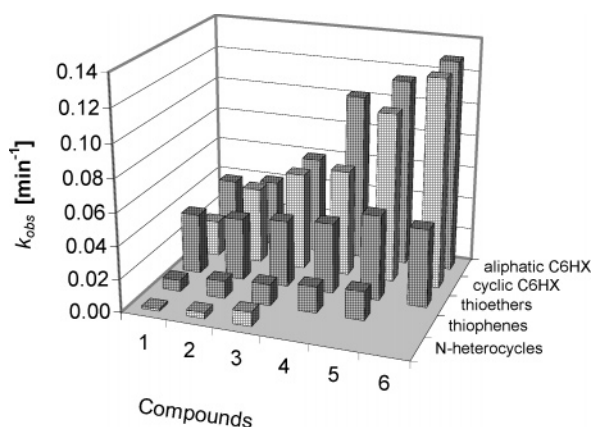


Figure 2. Comparison of aquasonolytic rate constants of various substrates. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C, 0.2 mM thioethers, 0.5 mM cyclic and aliphatic C<sub>6</sub>H<sub>x</sub>, 1.0 mM thiophenes and N-heterocycles. The numbers present the corresponding compounds noted in Table 1.

the transfer rate of substrate from bulk liquid to cavitation bubbles during the sonochemical destructions of trichloroethylene, tetrachloroethylene, benzene, and toluene.<sup>33</sup> Because of a higher Henry's Law constant or higher vapor pressure, more CCl<sub>4</sub> diffuses into the bubbles and undergo pyrolytic decomposition as the bubbles collapse than CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>.<sup>35</sup> 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.<sup>36</sup>

Figure 3 shows the aquasonolytic rate constant as a function of the Henry's Law constant for various model compounds under identical ultrasonic conditions. Although some exceptional cases exist, a higher Henry's Law constant generally results in a higher aquasonolytic rate constant within any compound group; it is even more obvious considering all model compounds. Hence, the transfer of organic substrate between bulk liquid and cavitation bubbles is essential for aquasonolysis. To identify the predominant factor on the transfer process, the roles of vapor pressure, octanol–water partition coefficient, and water solubility for the model compounds are further investigated.

**Role of Vapor Pressure of Substrate on Aquasonolytic Rate Constant.** Since pyrolysis of volatile organic substrates during the collapse of cavitation bubbles is generally regarded as its major pathway of sonication, the effect of volatility of substrates on aquasonolysis should be preferentially considered. Volatility describes how easily a substance will vaporize (turn into a gas or vapor bubbles here), and it is mostly dependent on its vapor pressure. Figure 4 shows the effect of the vapor pressure ( $P_v$ )

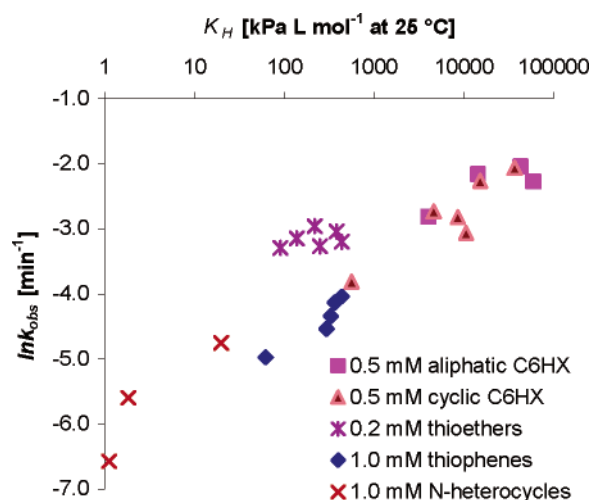


Figure 3. Aquasonolytic rate constant as a function of Henry's Law constant for volatile substrates. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C.

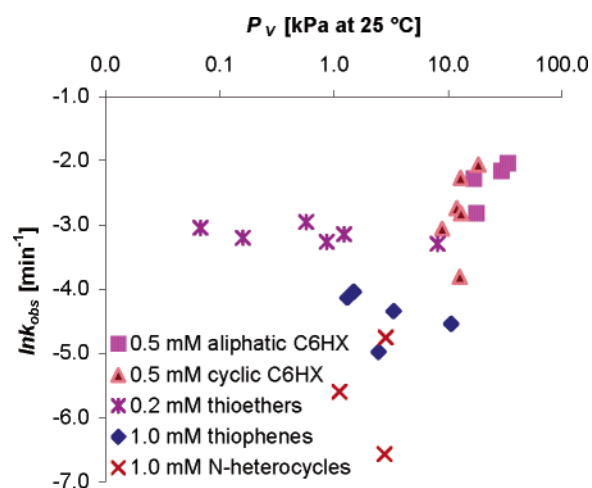


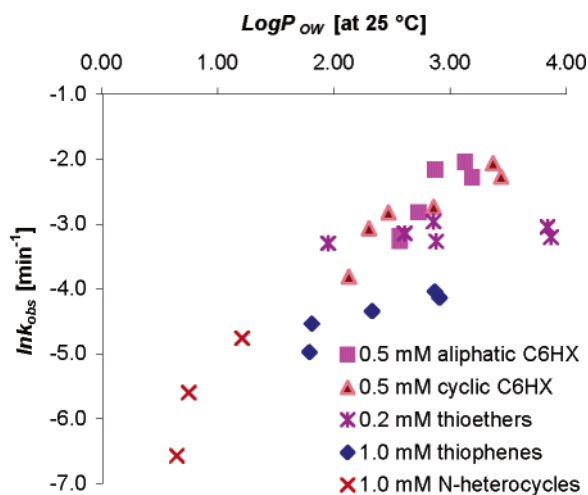
Figure 4. Effect of vapor pressure for volatile substrates on the aquasonolytic rate constant. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C.

on the aquasonolytic rate constants of various model compounds under identical ultrasonic conditions.

As shown in Figure 4, the aquasonolytic rate constant surprisingly shows an irregular variation with increasing vapor pressure within any compound group; it is even more obvious considering all model compounds. This result demonstrates that vapor pressure does not directly affect the transfer process and the aquasonolyses of the model compounds.

**Role of Hydrophobicity of Substrate on Aquasonolytic Rate Constant.** Hydrophobicity refers to the tendency of a substance to repel water or to be incapable of completely dissolving in water. Henglein et al. have observed that stronger hydrophobicity of organic solute increases the capacity for trapping OH radicals.<sup>30</sup> OH radical suppression is due to the enrichment of hydrophobic substrates in the bubbles and at the interfacial area. The hydrophobicity of an organic compound can be described fairly well by its octanol–water partition coefficient and water solubility in environmental chemistry.

(a) **Effect of Octanol–Water Partition Coefficient.** To further demonstrate the role of hydrophobicity, the effect of octanol–water partition coefficient ( $\log P_{ow}$ ) on the aquasonolytic rate constant for volatile substrates was investigated. Figure 5 shows the dependence of the aquasonolytic rate constant on the



**Figure 5.** Dependence of the aquasonolytic rate constant on the octanol–water partition coefficient for volatile substrates. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C.

octanol–water partition coefficient for the model compounds under identical ultrasonic conditions.

As shown in Figure 5, a higher octanol–water partition coefficient obviously results in a higher aquasonolytic rate constant within any compound group; it is even more obvious considering all model compounds, although a few exceptional cases still exist. Therefore, the hydrophobicity of volatile substrate affects the transfer process of volatile organic substrate between bulk liquid and cavitation bubbles and the aquasonolytic kinetics as well.

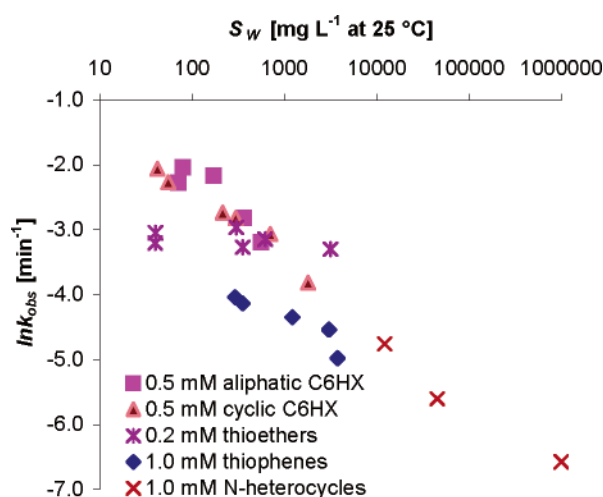
In the exceptional cases such as the aquasonolyses of thioethers, the vapor pressure and/or the reactivity of organic substrates with intermediates (i.e., free radicals, atoms, and active molecules) generated in situ in bulk liquid, to a certain extent, play a role simultaneously. For example, the hydrophobicity of dipropyl sulfide is higher ( $\text{Log}P_{\text{OW}} = 2.88$  at 25 °C), but its vapor pressure ( $P_{\text{V}} = 0.86$  kPa at 25 °C) is very low. Hence dipropyl sulfide is sonicated very slowly. The joint role of hydrophobicity and vapor pressure can be well demonstrated by Henry's Law constant as above-mentioned.

(b) *Effect of Water Solubility.* Since water solubility ( $S_{\text{W}}$ ) among various compounds spans very widely, it may more precisely reflect the dependence of aquasonolysis on the hydrophobicity of substrates than octanol–water partition coefficients. Figure 6 shows the dependence of the aquasonolytic rate constant on water solubility for the model compounds under identical ultrasonic conditions.

Obviously, a higher water solubility of substrate leads to a lower aquasonolytic rate constant within any compound group; it is even more obvious considering all model compounds. This result is completely consistent with the effect of octanol–water partition coefficient on the aquasonolytic kinetics of volatile substrate.

In consideration of the logarithmic scale of the X axis, as shown in Figure 6, water solubility has a profound influence on the aquasonolytic kinetics when the value is less than 1000  $\text{mg L}^{-1}$ . This effect is somewhat diminished when the value of water solubility reaches over 10 000  $\text{mg L}^{-1}$ . To demonstrate this conjecture, the impact coefficients of water solubility ( $F_{\text{s}}$ ) were calculated as follows

$$F_{\text{s}} = \frac{|k_{\text{max}} - k_{\text{min}}|}{|S_{\text{W}_{\text{max}}} - S_{\text{W}_{\text{min}}}|} \quad (\text{F2})$$



**Figure 6.** Dependence of the aquasonolytic rate constant on water solubility for volatile substrates. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C.

**TABLE 2: Impact Coefficients of Water Solubility on Aquasonolytic Rate Constant ( $\text{L mg}^{-1}\text{min}^{-1}$ )**

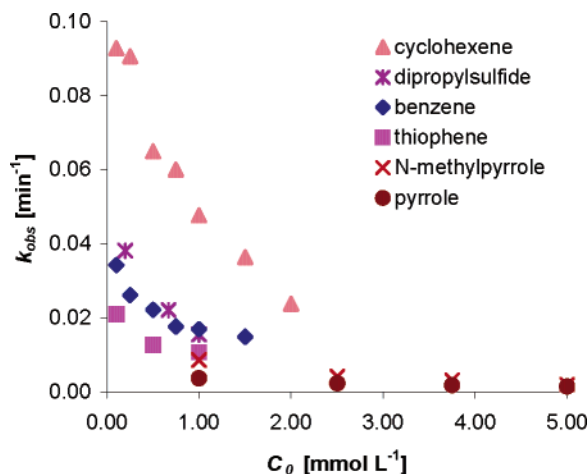
range of $S_{\text{W}}$ ( $\text{mg L}^{-1}$ )	30–400	300–700	600–4000	> 10 000
cyclic $\text{C}_6\text{H}_\text{X}$	$2.68 \times 10^{-4}$	$3.19 \times 10^{-5}$	$2.26 \times 10^{-5}$	
aliphatic $\text{C}_6\text{H}_\text{X}$	$2.49 \times 10^{-4}$	$9.35 \times 10^{-5}$		
thiophenes		$2.67 \times 10^{-5}$	$2.4 \times 10^{-6}$	
sulfides	$4.29 \times 10^{-5}$	$1.85 \times 10^{-5}$	$2.39 \times 10^{-6}$	
disulfides	$1.65 \times 10^{-5}$			
N-heterocycles				$6.07 \times 10^{-10}$

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

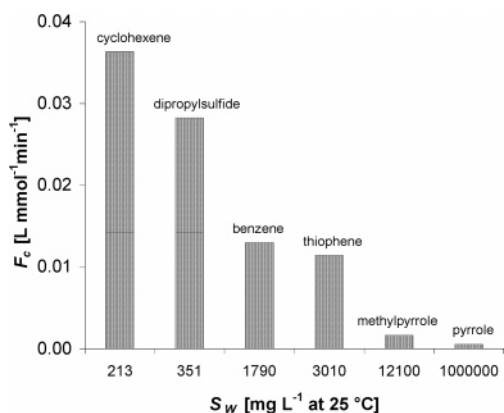
The results for the calculated impact coefficient of water solubility are summarized in Table 2. Indeed, water solubility can strongly influence the aquasonolytic rate for the model compounds when the solubility values are in the range of  $\sim 30$ – $400$   $\text{mg L}^{-1}$ . With a further increase in the solubility value, the effect of hydrophobicity on the aquasonolytic kinetics becomes less pronounced. When the water solubility reaches over 10 000  $\text{mg L}^{-1}$  (i.e., solubilities of pyrrole and pyridine), the effect of hydrophobicity on the aquasonolytic kinetics could be well neglected. In this case, the pyrolysis of hydrophilic organic compound hardly occurs, and the aquasonolysis proceeds very slowly.

This finding provides a complementary insight into the aquasonolytic mechanism for organic substrates. It demonstrates that hydrophobic volatile substrates are most readily sonicated in aqueous solution. By consideration that most products stem from pyrolyses of the model substrates during the collapse of cavitation bubbles in our previous investigations<sup>34,41</sup> rather than the oxidation of the organic substrates by OH radicals and/or  $\text{H}_2\text{O}_2$ , the pyrolysis of hydrophobic volatile substrate in collapsing bubbles and/or at the interfacial area dominates the sonolytic decomposition.

*Effect of Initial Concentration of Substrate on Aquasonolytic Rate Constant.* In general, the aquasonolytic rate constants tend to decrease as the initial concentration ( $C_0$ ) of substrate increases.<sup>19,31,32</sup> This trend has been also observed in our work and the results are shown in Figure 7. Since the ratio of specific heats of organic vapor is lower than that of air,<sup>19,21,22</sup> the organic compound entering cavitation bubbles decreases the collapse



**Figure 7.** Aquasonolytic rate constant as a function of initial concentration of substrate. Sonication conditions: 500 mL, 850 kHz, 40 W, 22 °C.



**Figure 8.** Impact coefficients of initial concentration of selected compounds with various water solubility.

temperature of cavitation bubbles. The higher the amount of organic vapor in the cavitation bubbles, the lower collapsing temperature of cavitation bubbles. This result demonstrates indirectly that the pyrolysis of organic substrate in cavitation bubbles is the predominant process for the aquasonolysis of hydrophobic volatile substrate.

Similar to the effect of water solubility, the effect of initial concentration of substrate on the aquasonolytic kinetics shows great difference among various compounds. The initial concentration influences the aquasonolysis of cyclohexene much more profoundly than pyridine. We postulate that this difference is possibly related to the hydrophobicity of organic substrate. To demonstrate this theory, the impact coefficients of initial concentration ( $F_c$ ) are calculated as follows

$$F_c = \frac{|k_{c_{\max}} - k_{c_{\min}}|}{|C_{\max} - C_{\min}|} \quad (\text{F3})$$

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

As shown in Figure 8, water solubility indeed plays an essential role in the effect of initial concentration for the model compounds on the aquasonolytic kinetics. The  $F_c$  value decreases with increasing water solubility. This result also indicates

that the pyrolysis of hydrophobic organic compound in collapsing bubbles is the predominant pathway of its sonication, while the pyrolysis of hydrophilic organic compound hardly proceeds in collapsing bubbles.

## Conclusions

The aquasonolytic rates of cyclic and aliphatic  $C_6H_X$ , thiophenes, thioethers, and N-heterocyclic compounds strictly follow pseudo-first-order kinetics. A higher Henry's Law constant for the model compounds results in higher aquasonolytic rate. The aquasonolytic rate constant varies irregularly with the change of vapor pressure of substrate. In contrast, the water solubility and the octanol–water partition coefficient strongly affect the aquasonolytic rate. The higher hydrophobicity of substrate, the higher aquasonolytic rate is observed. Furthermore, the aquasonolytic rate constant decreases with the increase of initial concentration of substrate. In conclusion, the transfer of volatile organic substrate between bulk liquid and cavitation bubbles is essential for the aquasonolysis. Although the volatility of organic substrate is the basic factor to influence the transfer process, it is not a determining factor to control the aquasonolytic kinetics for volatile substrates. It is indeed the hydrophobicity that dominates the transfer process and the aquasonolysis for volatile substrates.

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