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Ultrasonic Cleavage of Thioethers

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The rates of DPPH (diphenylpicrylhydrazyl) trapping and the sonolytical products obtained during the sonolysis of thioethers at normal and low temperature are reported. CS_2, lower sulfides, thiophene, and sulfurized species are the common products during the ultrasonic irradiations. Hydrocarbons are also obtained during the sonolysis of diallyl sulfide, diethyl disulfide, and dipropyl disulfide. Furthermore, aldehydes are obtained as oxidized species; SO_2 is found at 208 K. The principal sonochemical process appears to be the cleavage of C−S or S−S bond with secondary combinations and rearrangements. DPPH has been used to probe the sonolytical potential of thioethers. The results show a good correlation between the rates of DPPH trapping and the vapor pressures of thioethers. In conclusion, a lower vapor pressure results in a higher sonolytical rate. The sonochemical behaviors of thioethers have strong qualitative similarities to the pyrolysis.

Introduction

The mechanism and kinetics of the sonolysis of organic chemicals in aqueous solutions have been extensively studied since 1929.[1,2] Although it is essential to realize the sonochemical behavior of organic liquids, only a few examples of homogeneous nonaqueous sonications have been reported since the 1950s.[3−7]

The origin of sonochemistry is acoustic cavitation. Organic liquids with high vapor pressure greatly diminish the intensity of cavitational collapse.[3,8] In 1983, Suslick et al. reported the sonochemistry of alkanes.[8] They illustrated that decreasing vapor pressure of the solvent increases the intensity of cavitational collapse, the peak temperature of the collapse, and the rates of sonochemical reactions. Primary products were H_2, CH_4, C_2H_2, and lower 1-alkenes. Up to 1999, Mizukoshi et al. reported the effect of the vapor pressure and evaporation on the sonolysis of organic liquids.[9] The hydrocarbons most efficiently decomposed at the vapor pressure range of 0.1−0.5 Torr, whereas the most efficient vapor pressure for the sonolysis of alcohols was about 15 Torr. The main products were H_2, CH_4, C_2H_4, and C_2H_2 from hydrocarbons, and H_2, CH_4, C_2H_4, CO and aldehydes from alcohols. Other researchers demonstrated that the sonochemical polymerization of benzene derivatives, the sonolysis of $BrCCl_3$, and the ultrasound-induced cracking of some aromatic and naphthenic hydrocarbons were quite similar to the pyrolysis.[10−12]

DPPH (diphenylpicrylhydrazyl) 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.[8,9,11] Thus, the rates of DPPH trapping in sonolysis can be used to show both the formation of free radicals and the potential of sonolysis of organic liquids.

The ultrasonic desulfonylation of cyclic sulfones in toluene has been reported. Ultrasonically dispersed potassium promoted the cleavage of C−S bond and the extrusion of sulfur dioxide from di- and trisubstituted 3-sulfolenes to give the corresponding dienes.[13,14] This paper reports the rates of DPPH trapping, sonolytical products, and the effect of the liquid temperature, vapor pressure, and ultrasonic intensity on the sonolysis of thioethers. On the basis of the references of the pyrolysis of thioethers, the mechanisms of the sonolysis of thioethers are proposed by seeking the enhancement effect of low temperature on sonolytical rates and yields of products.

Experimental Section

Chemicals. Diethyl sulfide (DES; Aldrich, 98%), diallyl sulfide (DAS; Aldrich, 97%), dipropyl sulfide (DPS; Aldrich, 97%), dibutyl sulfide (DBS; Fluka, 98%), diethyl disulfide (DEDS; Aldrich, 99%), dipropyl disulfide (DPDS; Aldrich, 98%), and diphenylpicrylhydrazyl (DPPH, Fluka, 85%) were used as received.

Ultrasonic Device and Irradiation Conditions. This device consists of an ultrasonic processor with a titanium probe (UP200S, Dr. Hielscher GmbH, Stuttgart) and a cylindrical glass reactor. The ultrasonic processor works at 24 kHz under the atmosphere of dry air. The acoustic intensity was determined through caloric measurements and can be regulated (15−45 W cm^{-2}). The temperature of the bulk liquid is maintained constant by circulating cooling water, or controlled by a mixture of dry ice and 2-propanol to keep a low temperature (208 K). The volume of each sample irradiated was 3 mL.

A 60.0 mmol L^{-1} DPPH solution was prepared by dissolving 139.0 mg DPPH (85%) in 5.0 mL of methanol. A 20 or 50 μL aliquot of the 60.0 mmol L^{-1} DPPH solution was added to a 3.0 mL solution of thioethers to detect the rate of DPPH consumption.

Analysis. Quantitative and qualitative analyses were carried out by GC/MS. GC conditions: Agilent Technologies GC 6890N/MSD 5973 Network with MSD Chemstation D: 01.00. Carrier gas: He (8.7 psi, 1.2 mL min^{-1}). HP-5MS capillary column: 30 m × 0.25 mm × 0.25 μm. GC oven temperatures were kept constant during the first 5 min at 35 °C, then ramped up to 250 °C with 10 °C/min, and kept constant for 3.5 min.

Absorption spectra of DPPH in thioethers were recorded with a Shimadzu UV-2102PC spectrophotometer ($\lambda_{max} = 517$ nm).

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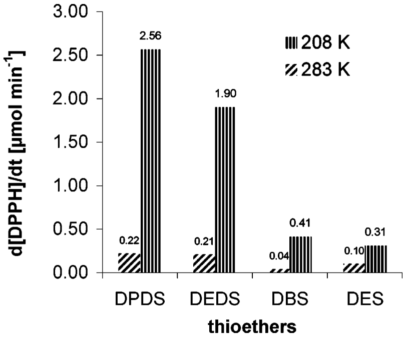


Figure 1. Rates of DPPH trapping in thioethers at 208 and 283 K (1.0 mmol L^{-1} DPPH, 3.0 mL, 24 kHz, 30 W cm^{-2}).

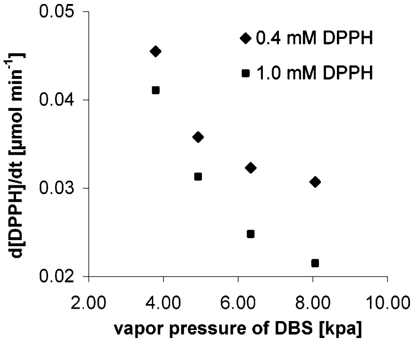


Figure 2. Effect of solvent vapor pressure on rate of DPPH trapping in DBS (3.0 mL, 24 kHz, 30 W cm^{-2}).

The corresponding pure thioethers were respectively used as the blank solution.

Results and Discussion

Effect of Liquid Temperature on Rates of DPPH Trapping in Thioethers. The rates of DPPH trapping in DES, DBS, DEDS, and DPDS at 208 and 283 K were observed and compared as shown in Figure 1. In all thioethers that have been studied, 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 identical temperatures. Obviously, the low liquid temperature (i.e., low vapor pressure of solvents) increases the rates of DPPH trapping and enhances the sonolysis of thioethers as well.

To further proof the effect of the vapor pressure of the solvent, the rates of DPPH trapping were investigated at different temperatures in dibutyl sulfide. Figure 2 shows the effect of vapor pressure of solvent on the rates of DPPH trapping at various initial concentrations in DBS. Vapor pressures were calculated using data from the NIST Webbook.[15] Indeed, the rates of DPPH trapping decrease as the vapor pressures of DBS increase.

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:[8]

$$T_{\mathrm{max}} = \frac{T_0 P_{\mathrm{a}}(\gamma - 1)}{P_{\mathrm{v}}} \qquad \text{(i)}$$

where T_0 is the liquid temperature, P_a is the acoustic pressure at initiation of collapse, γ is the ratio of specific heats, and P_v is 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.

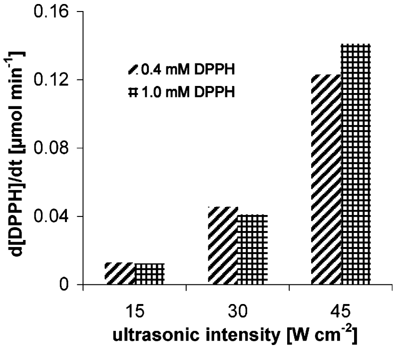


Figure 3. Effect of ultrasonic intensity on the rate of DPPH trapping in DBS (3.0 mL, 24 kHz, 283 K).

If $P_{\mathrm{a}}^{283\mathrm{K}} \approx P_{\mathrm{a}}^{298\mathrm{K}}$,

$$T_{\mathrm{max}}^{283\mathrm{K}}/T_{\mathrm{max}}^{293\mathrm{K}} = \frac{283 P_{\mathrm{a}}^{283\mathrm{K}}(\gamma - 1)}{3.8} \div \frac{298 P_{\mathrm{a}}^{298\mathrm{K}}(\gamma - 1)}{8.3} = 2.07 \qquad \text{(ii)}$$

It appears that the maximum collapsing temperature at 283 K is over twice as high as that at 298 K. Arrhenius equation ($k = Ae^{-E_{\mathrm{a}}/RT_{\mathrm{max}}}$) was often employed to explain the reaction kinetics in the bubble as[3,4,8]

$$\ln k = \ln A - \frac{E_a P_v}{R T_0 P_a(\gamma - 1)} \qquad \text{(iii)}$$

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

Effect of Ultrasonic Intensity on Rates of DPPH Trapping. Because the collapse time, the temperature, and the pressure of the cavitation bubbles are dependent on the ultrasonic pressure amplitude, the influence of ultrasonic intensity on the sonochemical rates was investigated. In general, 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.[4] Figure 3 shows the effect of ultrasonic intensity on the rates of DPPH trapping at various initial concentrations in dibutyl sulfide.

Clearly, increasing ultrasonic intensity increases the rate of DPPH trapping. Meanwhile, the effect of the initial concentration of DPPH may be negligible, indicating that DPPH trapping takes place in bulk liquid.

Primary Analysis of Products during the Sonolysis of Thioethers. Most products are directly formed by the pyrolysis during the collapse of the cavitation bubbles. It has been reported that H_2S, CH_4, C_2H_4, C_2H_6 and H_2 can be formed during the pyrolysis of methyl benzyl sulfide (CH_3SCH_2Ph), dimethyl sulfide (CH_3SCH_3), dimethyl disulfide (CH_3SSCH_3).[16]

Because gaseous species cannot be detected by our sample method and GC-columns, heavier species were considered in this work. Due to the higher vapor pressure of DES, no products were found from DES during the ultrasonic irradiation at normal temperature. However, other sulfides and disulfides can undergo sonolysis at normal temperature, although the yields are relatively low. At low temperature, the yields of most products increased greatly. Table 1 shows the sonolytical products of thioethers at low temperatures.

On the basis of Table 1, CS_2, lower sulfides, and sulfurized species are the most common sulfur-containing products occurred by cleavage of bonds. Disulfides or trisulfides can readily

TABLE 1: Products from the Sonolysis of Thioethers at Low Liquid Temperature (3 mL, 24 kHz, 30 W cm^{-2}, 208 K, 240 min Sonication)

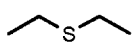
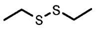
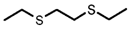
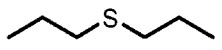
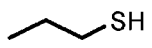
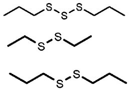
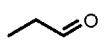
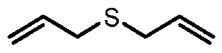
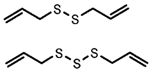
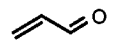
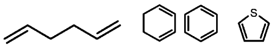
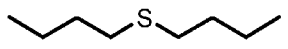
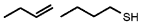
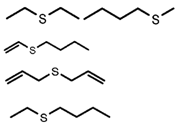
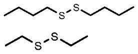
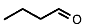
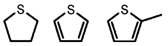
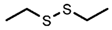
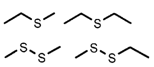
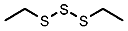
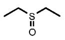
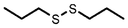
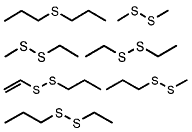
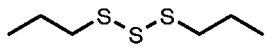
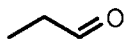
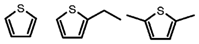
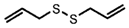
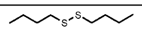
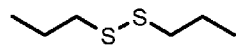
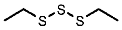
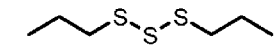
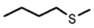
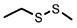
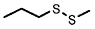
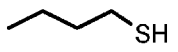
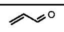
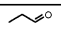
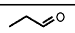
	Cleavage of bonds	Sulfurized	Oxidized	Other radical reaction
	CS_2 		SO_2	
	CS_2  C_3H_6S 		SO_2 	 $C_5H_{10}S$
	CS_2 C_3H_6S	 $C_4H_{10}S_2$ $C_4H_8S_2$ $C_6H_8S_2$	SO_2  C_5H_8O	C_4H_6 C_4H_4 C_4H_2 C_5H_6 C_5H_8 C_6H_8 C_7H_{12}  C_5H_8S $C_6H_{10}S$ $C_6H_{10}S_2$
	CS_2  		SO_2 	
	CS_2  	 $C_4H_{10}S_4$	SO_2 	C_4H_6 C_4H_4  S_8 C_4H_8S $C_4H_8S_2$ $C_5H_{12}S_2$
	CS_2  	 $C_2H_2S_4$ $C_2H_6S_3$	SO_2 	C_4H_6 C_6H_{10} C_6H_{12} C_6H_{14} $C_5H_{10}S$ $C_5H_{12}S$  $C_4H_8S_2$ $C_6H_{12}S$ S_8

TABLE 2: Enhancement Factors of the Low Temperature on the Formation of Typical Products (3 mL, 24 kHz, 30 W cm^{-2}, 240 min Sonication at 208 and 283 K Respectively)

Substrates	DAS	DBS	DPS	DES	DEDS	DPDS
Sulfurized species						
F_e	0.9	+	0.3	-	0.7	0.4
low sulfides	C_3H_6S			C_2H_4S		
F_e	1.7	+	+	+	0.8	0.9
Thiols				-	-	-
F_e	-	+	47.6			
Aldehydes				-	-	
F_e	2.8	1.0	+			1.2
CS_2	+	+	106.5	+	2	2.8
Thiophene	+	+	+	-	+	1.8
SO_2	+	+	+	+	+	+
S_8	-	-	-	-	5.3	3.1

[a] $F_e > 1$: enhanced effect. −: no detectable product at 208 and 283 K. +: detectable product only at 208 K.

be formed during the sonolysis 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 diallysulfide, such as 1,5-hexadiene, 1,3-cyclohexadiene, and benzene. Meanwhile, some oxidized products are detected, i.e., SO_2 and aldehydes. All of these products demonstrate that thioethers undergo pyrolysis and complex radical reactions during ultrasonic irradiation.

To elucidate the enhanced effect of low temperature (i.e., low vapor pressure of solvents) on the formation of products, the enhancement factors of low temperature are calculated with eq iv, and the results are listed in Table 2,

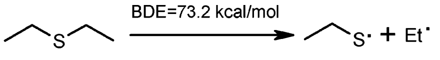
$$F_e = \frac{(A_{lt} - A_{l0})/t_l}{(A_{rt} - A_{r0})/t_r} \qquad \text{(iv)}$$

where A_{lt} is the GC peak area of a selected product at a given reaction time at 208 K, A_{l0} is the GC peak area of a selected product at the initial time at 208 K, t_l 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.

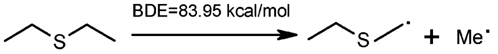
According to Table 2, the low temperature (low vapor pressure of solvent) enhances the cleavage of C−C and C−S bonds, and increases the yields of low sulfides, thiols, CS_2, thiophene, oxidized products, and S_8 as well. Especially, SO_2, CS_2, and thiophene can be only generated during the sonolysis of sulfides at low temperature. This demonstrates the enhancement effect of low temperature. However, the yields of sulfurized products cannot increase at 208 K. Because the C−S bond is the weakest bond within thioether molecules,[17] and most thioethers have relatively low vapor pressures at 283 K, the maximum collapsing temperature may be high enough for the dissociation of C−S bonds at 283 K.

Reaction Mechanisms of the Sonolysis of Thioethers. To the best of our knowledge, no report about the sonolysis of thioethers has been given yet. Hence, comprehending the pyrolytical mechanisms of thioethers would help us understanding their mechanisms of sonolysis. On the basis of the present experimental results and studies on pyrolytical mechanisms, sonolytical mechanisms of thioethers are suggested as follows:

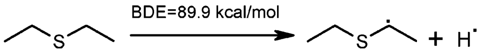
(I) Unimolecular Dissociation and Combination of Free Radicals. According to the bond dissociation energies (BDEs), the bonds of C−S, S−S, or C−C of thioethers are systematically cracked under the ultrasonic irradiation. Then the radicals are recombined with each other. Montgomery et al. reported the BDEs of diethyl sulfide as reactions 1−4[17] (1 kcal = 4.184 kJ).



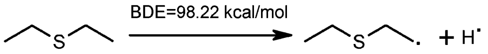
(1)



(2)



(3)



(4)

However, due to the higher vapor pressure of DES (8.03 kPa at 298 K), no sulfurized product, thiol, thiophene, and dehydrogenated products were obtained from the sonolysis of diethyl sulfide even at low temperature; SO_2 and a small amount of CS_2 were found 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) underwent the cleavage of C−S, S−S, and C−C bonds, and even the cleavage of C−H bond at 283 K. Vapor pressures were taken from SRC PhysProp Database.[18]

The formations of disulfides, thiols, lower sulfides, and hydrocarbons during the sonolysis of thioethers were readily explained by reactions 5−10:

$$R{-}S{-}R \xrightarrow{)))} RS^\bullet + R^\bullet \tag{5}$$

$$2\,RS^\bullet \rightarrow RSSR \tag{6}$$

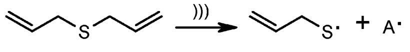
$$2R^\bullet \rightarrow R{-}R \tag{7}$$

$$M + RS^\bullet \rightarrow M_{-H}^\bullet + RSH \tag{8}$$

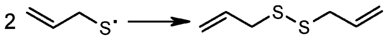
$$M + RSR_1^\bullet \rightarrow M_{-H}^\bullet + RSRH \tag{9}$$

$$M + R^\bullet \rightarrow M_{-H}^\bullet + R\,H \tag{10}$$

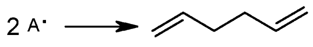
The products from the sonolysis of diallyl disulfide prove the recombination of free radicals very clearly, i.e., 1,5-hexadiene and diallyl disulfide (reactions 11−13):



(11)

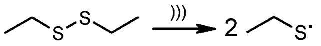


(12)

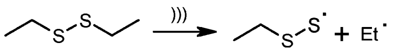


(13)

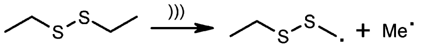
Similarly, disulfides additionally undergo the dissociation of the S−S bond. This is demonstrated by the radical mechanism, which forms diethyl sulfide, methyl ethyl sulfide, methyl ethyl disulfide, dimethyl disulfide, and diethyl trisulfide during the sonolysis of diethyl disulfide (reactions 14−16).



(14)

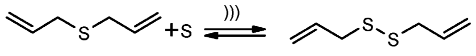


(15)

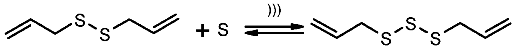


(16)

(II) Sulfuration. Not only the recombination of two RS radicals forms sulfurized products, but also sulfide can react with S_8 or S atoms. Baechler et al. reported the sulfuration of diallyl sulfide with S_8 in Me_2SO-d_6 at 353−363 K.[19] Green et al. also reported that S atoms reacted with CH_3SCH_3 to generate elemental sulfur and CH_3SSCH_3 as major primary products.[20] Under ultrasonic irradiation, S atoms may be released by the sonolysis of thioethers.[13,14] This result may be used to the ultrasonic desulfurization of sour crude oil. Hence, it is possible that S_8 is formed by combination of S atoms. Trisulfide would also be produced by sulfuration of disulfide (reactions 17−18):

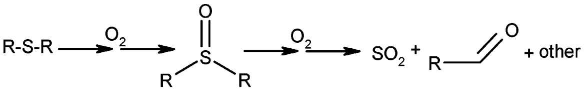


(17)



(18)

(III) 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. Spurlock and Reifsneider found that dibutyl sulfoxide was the principal product of the aquasonolysis of dibutyl sulfide. Meanwhile, butanesulfonic acid, dibutyl sulfone, butyric acid, and carbon monoxide were the minor products.[21,22] In this investigation, SO_2 and aldehydes were found during the sonolysis of thioethers under an atmosphere of dry air. Diethyl sulfoxide is obtained during the sonolysis of diethyl disulfide. The oxidation pathways are proposed as reaction 19. In addition, thiols are also oxidized to disulfides by molecular oxygen:[22]



(19)

$$2RSH + {}^{1}/_{2}O_2 \rightarrow RSSR + H_2O \qquad (20)$$

Conclusions

DPPH has been successfully used to probe the sonolytical potential of thioethers. The rates of DPPH trapping are strongly dependent on the liquid temperature. The rates of DPPH trapping in thioethers are much higher at 208 than at 283 K and are higher in disulfides than in sulfides at identical temperatures. Thus, the low temperature (i.e., low vapor pressure of thioethers) can enhance the sonolysis of thioethers. In addition, the higher ultrasonic intensity also results in higher rate of DPPH trapping.

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

The low temperature can increase the yields of low sulfides, thiols, CS_2, thiophene, and oxidized products as well. Furthermore, the low temperature can cause the formations of SO_2, CS_2, and thiophene. This demonstrates the enhancement effect of low temperature. However, the low temperature cannot increase the yields of sulfurized products, because most thioethers are readily sulfurized under ultrasonic irradiation at normal temperature.

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