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journal or publication title	滋賀医科大学基礎学研究
volume	11
page range	15-21
year	2001-03
その他の言語のタイトル	ダイオキシンモデル化合物の超音波分解 ダイオキシン モデル カゴウブツ ノ チョウオンパ ブンカイ
URL	http://hdl.handle.net/10422/1237

ULTRASONIC DEGRADATION OF A DIOXIN-TYPE MOLECULE

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Abstract. This paper presents some results of the research work aiming to find out a method to decompose a dioxin-like compound. As a model, 4-chlorodiphenylether was chosen. Ultrasound energy in combination with Raney Ni catalyst was employed for this research. The best conversion of 4-chloro-diphenylether (>95%) was achieved for 20 kHz at 60 °C and 0.1g Raney Ni. This combination of ultrasound and a catalyst is a promising one as a possible technique for dioxin decontamination.

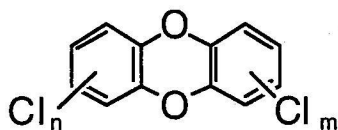
Keywords: sonochemistry, dioxin, environment, decontamination.

INTRODUCTION

Environmental pollution caused by chlorinated organic compounds is one of the most acute problems of our century. Chlorinated pollutants with different structures and molecular weights, ranging from organic solvents up to chlorophenols, PCBs and dioxins have been detected in the atmosphere as well as in soil and water [1].

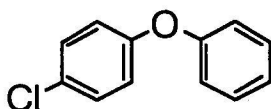
Chemical reactions in ultrasonic field are the consequence of extreme conditions generated by the collapse of cavitation bubbles. During the collapse, high temperature (~5000 °K) and pressure (~1000 atm) are generated and these conditions lead to pyrolysis of almost all molecules that enter the bubble [2].

Efforts were done to use the power of ultrasound for degradation of chlorinated compounds. A wide range of chlorinated organic substances was subjected to ultrasound action with the hope of total degradation. Studies were carried out on the sonochemical destruction of carbon tetrachloride [3,4,5,6,7], chloroform [6,7,8,9], methylene chloride [9], 1,2-dichloroethane [9,10,11], 1,1,2,2-tetrachloroethane [10], trichloroethane [11], trichloroethylene [6,7,9,10,12,13], tetrachloroethylene [6,9,10], chlorofluorocarbons [14], chlorobenzene [10,13,14], bromobenzene [15,16], *o*-chlorotoluene [17], polycyclic aromatic hydrocarbons [18,19,20], *o*, *m*, and *p*-chlorophenols [21], 2,4,6-trichlorophenol [22], pentachlorophenol [23,24,25], pentachlorophenolate [25], etc. Among pollutants one of the most dangerous and difficult to be destroyed is the class dioxins with general formula:



$n + m = 1, 2, \dots, 8$
dioxins

The present study is focused to the sonochemical decomposition of dioxin type molecules, and as model the 4-chlorodiphenylether (CDPE) was chosen:



Examining this model one can see that the O, aromatic ring and Cl sequence is similar to some dioxins and therefore its behavior under ultrasonic field could be extended to real dioxin molecules.

EXPERIMENTAL

Apparatus:

Three kinds of ultrasonic equipments were used in this study:

- 1). 20 kHz Sonicator XL2020 Heat System, 500 W, operated at 20% of power output; tip area = 0.877 cm² (direct immersion type);
- 2). 200 kHz multiwave ultrasonic generator Kaijo, TA 4021; 200W input power, oscillator diameter = 65 mm (bath type);
- 3). 35 kHz Transonic T420 cleaning bath, 45 W total power.

A Shimadzu GC-14A gas chromatograph with a 2 m long, 4 mm diameter, PEG 20M (5%) column was employed for analysis.

Materials:

Raney Ni and 4-chlorodiphenylether were purchased from Wako;

Procedure:

4-Chlorodiphenylether (CDPE) was dissolved in methanol. Raney Ni and aqueous NaOH solution (1.5 g/L) were mixed for 2-3 minutes, then CDPE in methanol was added. The final concentrations of CDPE were 2505, 228 and 33 ppm. Raney Ni used in each experiment was 0.1 g. The concentration of NaOH was 37.5 mmol/L. In each case sonication was performed for 2 hours at 40 °C. One experiment was also run at 60 °C.

After sonication the organic materials were extracted with methylene chloride, then the aqueous layer was acidified and extracted again. The organic extracts were combined and evaporated to 1-5 cm³. The residue was analyzed by gas chromatography using tetradecane as an inter-

nal standard.

RESULTS AND DISCUSSION

For the 40 °C experiments with different equipments and initial concentrations of CDPE, and 0.1 g Raney Ni, the results are given in Tables 1-3. The figures are shown in mass percent.

Table 1.

20 kHz	CDPE	Ph-O-Ph	Ph-OH	cyclohexanol
2505 ppm	37	41	0	1.5
228 ppm	90	7	3	0
33 ppm	73	7	4	0

Table 2.

200 kHz	CDPE	Ph-O-Ph	Ph-OH	cyclohexanol
2505 ppm	77	6	0	5
228 ppm	19	45	25	1
33 ppm	86	3	1	0

Table 3.

35 kHz	CDPE	Ph-O-Ph	Ph-OH	cyclohexanol
2505 ppm	64	24	0	0
228 ppm	40	32	28	1
33 ppm	90	9	2	0

For 60 °C experiments at different frequencies and initial concentration of CDPE of 2505 ppm and 0.1g Raney Ni, the results are given in Table 4.

Table 4.

2505 ppm	CDPE	Ph-O-Ph	Ph-OH	cyclohexanol
20 kHz	3.5	30	0	21
200 kHz	26	51	0	27
35 kHz	70	16	0	12

For comparison, the silent reaction by replacing ultrasonic energy with a magnetic stirrer was performed using similar conditions as for sonochemical reaction. The results of silent reaction are given in Table 5.

Table 5.

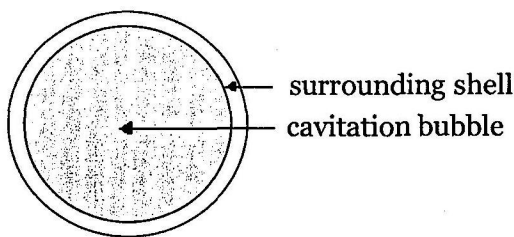
Silent	CDPE	Ph-O-Ph	Ph-OH	cyclohexanol
2505 ppm	71	11	2	1.8
228 ppm	45	28	24	0.6
35 ppm	84	7	3	0.4

Almost all sonochemical reactions occur inside the cavitation or surrounding shell of bubbles, or are originated here. The cavitation bubble contains mainly the solvent vapor as well as dissolved gas and reagents. The more volatile the reagents dissolved in the solvent are, the higher is their concentration inside the bubble. Even in the case of low volatility there is some reagent inside the bubble.

Examining the results from the Tables, one can see that at 40°C and higher concentration of CDPE (2505 ppm) the most effective process occurs at low frequency. Even in the case of a cleaning bath that has low power (~1 W) the advancement of degradation of CDPE is better than at 200 kHz.

However, the decomposition reaction of CDPE occurs even in the absence of ultrasonic field, showing that Raney Ni catalyst promotes the hydrogenolysis of the chloroderivative. Special attention deserves the reactions performed at 60 °C, when the hydrogenation process becomes important, proving that the inside cavitation reaction increases with the volatility.

It is reasonable to interpret these results by the fact that the decomposition reaction of CDPE takes place inside cavitation bubbles, in the surrounding shell as well as the bulk liquid. Taking into account that CDPE is a rather nonvolatile compound its concentration inside bubbles is low.



Zones of higher concentration during cavitation

Indeed, if the initial concentration is high and only a limited number of molecules enter cavitation, the ratio of entered/total CDPE's molecules is very small. By contrast, at lower concentration the number of entered molecules is similar or almost similar, but the total number is smaller, leading to a greater ratio. This fact is well described by the behavior of CDPE at 200 kHz and 228 ppm, when both processes inside and outside bubbles occur simultaneously. The result is a better decomposition of the starting material. This means that for higher concentration of CDPE two reactions took place: sonochemical decomposition and hydrogenolysis in bulk liquid.

Further lowering the initial concentration leads to less and less molecules entering the cavitation and, therefore, a diminished reaction inside cavitation. In the same time the surrounding shell has lower CDPE concentration and therefore the reaction in both these regions is diminished. The overall effect is lower conversion of CDPE into harmless compounds.

An argument in favor of the above allegations is the result from the 60 °C experiments. Indeed, when the temperature rises, the volatility of CDPE increases and the amount of molecules entering cavitation increases too. This enhances the inside bubble reaction as well as the interface one. Cyclohexanol is produced in the largest percent in this experiment, demonstrating that inside cavitation the bond cleavage is followed by phenol formation and its reduction in the interface and the bulk liquid.

Our explanation of the present results is that we have inside cavitation decomposition of CDPE as a monomolecular reaction, while the reactions occurring in the surrounding shell and bulk liquid are bimolecular. This means that inside cavitation CDPE suffers pyrolysis while outside cavitation in the interface and in the bulk liquid oxidation takes place, by HO radicals that are copiously generated from the water vapor during the collapse, as well as hydrogenation with the hydrogen atoms generated by the catalyst.

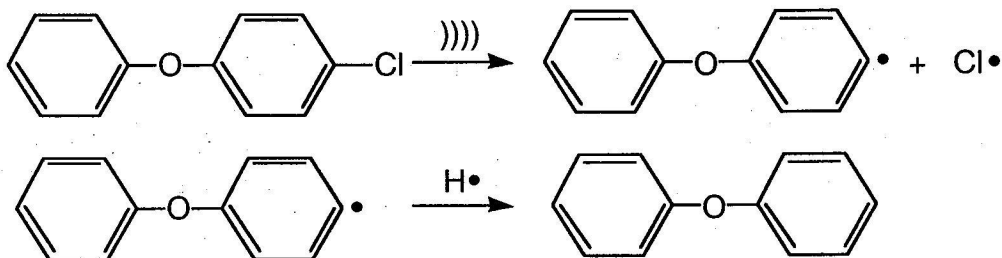
REACTION MECHANISMS

The first reaction that occurs, regardless the reaction site, inside or outside cavitation, is dechlorination of CDPE. The reaction pathway is however different inside and outside the bubble.

Inside cavitation:

There are two processes that occur inside the cavitation bubbles during their collapse: water decomposition leading to HO radicals and hydrogen atoms, and pyrolysis of the chlorinated compound.

The reaction inside the bubble is a monomolecular one, namely the pyrolysis of CDPE, leading to C - Cl bond cleavage:



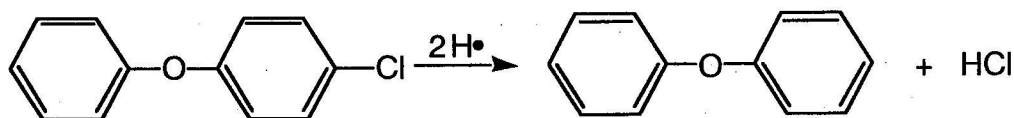
The diphenylether radical extracts hydrogen or reacts with the hydrogen generated by water decomposition inside cavitation, leading to diphenylether as the main reaction product. The chlorine atom is trapped by the NaOH solution. The inside cavitation reaction is therefore responsible mainly for diphenylether production.

The second major reaction product is phenol (sodium phenolate due to the alkalinity of the medium) and it could be obtained by further splitting of diphenylether radical. Phenol cannot suffer further decomposition because the high pH of the bulk solution forbids its entering the cavitation.

The largest amount of phenol is formed in the 200, 35 kHz as well as in the silent experiments. These results suggest the possible formation of phenol by CDPE hydrogenolysis outside cavitation.

Outside cavitation:

As was mentioned before, outside cavitation a bimolecular process occurs, namely the reaction of CDPE with the hydrogen generated by the Raney Ni catalytic system.



This reaction produces diphenylether and by further hydrogenation of this one, phenol as well as cyclohexanol. The silent reaction proves this by its products mentioned above.

In our experimental system the CDPE decomposition is a consequence of both processes: sonochemical and silent one. In the sonochemical process there is a monomolecular reaction inside the cavitation bubbles and a bimolecular one outside the cavitation bubbles. The latter operates for the silent reaction too.

CONCLUSIONS

The results of the work presented in this paper could be summarized in the following conclusions:

- Decomposition of a dioxin-like compound is possible using a combination of ultrasonic energy and a catalyst (Raney Ni).
- By choosing the right ultrasonic frequency, temperature as well as initial concentration of the chlorinated compound, a high conversion could be achieved: 20 kHz, 60 °C gives 96.5% conversion of CDPE. The power of ultrasound to promote decontamination is clearly shown by the 60 °C experiments.
- This research work demonstrates that it is possible to use the ultrasonic technique in connection with a catalytic system to attack the dioxin decontamination problem.

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