

Sonolysis of chlorobenzene in the presence of transition metal salts

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Abstract: Sonolysis of aqueous solution of chlorobenzene at 200 kHz frequency in the presence of transition metals chlorides was investigated. Through analyzing the nature and distribution of the products detected in the reaction mixture, a new mechanism of sono-degradation is advanced. Depending on the metals used and their behavior during sonolysis, we were able to discriminate between inside and outside cavitation bubble mechanisms. Iron and cobalt chlorides, which could undergo redox reactions in the presence of HO radicals generated ultrasonically, give higher amounts of phenolic compounds compared with palladium chloride that undergoes a reduction to metal. Palladium reduction takes place in bulk solution and therefore all organic reactions that compete for hydrogen must occur also in bulk solution. Accordingly, palladium can be a useful tool in determining the reaction site and the decomposition mechanism of organic compounds under ultrasonic irradiation.

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1 Introduction

Sonochemistry, defined as the effects produced by subjecting a chemical reaction to the ultrasound waves, has seen a constant development in the last ten years. The ultrasounds, with frequencies roughly between 15 kHz and 10 MHz, cause effects on chemical reactions. The mechanisms that originate these effects are known as “acoustic cavitation”. Shortly,

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this means the creation of bubbles within a liquid followed, after several acoustic cycles, by a violent collapse that releases, locally, a tremendous amount of energy in the order of ~ 5000 K and ~ 1000 atm temperatures and pressures, respectively [1]. In the last few years the use of sonochemistry as a degradation technique for organic pollutants has blossomed [2, 3, 4, 5, 6]. Under ultrasonic irradiation, organic compounds are degraded by two mechanisms: volatile and apolar solutes such as chloroform and chlorobenzene are mainly pyrolyzed in the cavitation [7, 8], while polar compounds are oxidized with reactive species formed by dissociation of water in bulk solution [9]. Chlorinated compounds are common contaminants of water. A series of studies have already been devoted to the sono-degradation of aqueous solution of halo-derivatives as: chlorophenols [10], *o*-chlorotoluene [11], trichloroethylene [12], dichlorobenzenes [5].

Degradation by sonication is a very simple and appealing method but is a rather costly process for industrial applications. In order to minimize the energy consumption, attempts were made to increase the process efficiency by some additives. Several studies dedicated to the effect of added solid catalysts on sonolysis: Raney nickel, vanadium pentoxide, silver, platinum oxides [9] and alumina particles [13] showed some improvement. In order to enhance the degradability of the chlorinated pollutants during sonication, some water-soluble compounds, i.e. Fenton's type compounds, were added to the water solution and were found to degrade effectively chlorobenzene, chlorophenols and dichlorobiphenyls [14, 15].

In previous papers we have shown that by using metal salts it is possible to have a better knowledge of the sono-degradation mechanism of chlorobenzene (CB), mainly concerning the intermediates dissolved in water [16, 17].

The present study is focused on the CB decomposition in the presence of metallic chlorides, under ultrasonic irradiation in order to gain more information on the chlorobenzene chemical degradation mechanism under ultrasound, the type of compounds formed in aqueous solution during sonication and the role of metals and chloride anion, if any. To know the decomposition chemistry of an organic pollutant is of crucial interest in environment decontamination. The present work brings about some new knowledge on aromatic halide sono-decomposition mechanism.

2 Experimental

2.1 Materials

Chlorobenzene (CB) (>99% purity), Pd(II) chloride (99%), Fe(II) chloride tetrahydrate (99.9%), Fe(III) chloride hexahydrate (99.9%) and Co(II) chloride hexahydrate (99.5%) were purchased from Wako Chemicals, and used as received. The solution was prepared by dissolving around 0.9 mmols of CB in deionized water to make a solution of 1000 ml. The metal chlorides were added just before sonication.

2.2 Sonolysis

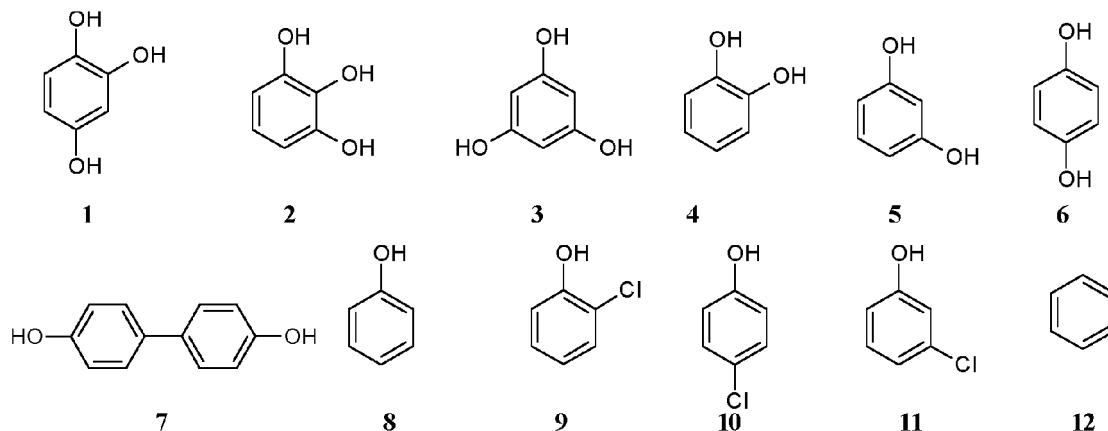
Sonifications of 100 ml solutions were performed in 150 ml reaction cells using a 200 kHz Kanjo Denki Model 4021 sonicator, having a submersible transducer. During the irradiation the vessel was closed. The ultrasonic irradiation was performed in a temperature-controlled water bath at 20 °C, with a constant water level. A schematic diagram of the experimental setup is given in figure 1.

2.3 Analysis

Every 10 minutes aliquots of 1 ml were taken from the reaction vessel. Analyses were performed on a Shimadzu HPLC Chromatograph equipped with a UV detector. A Hikarisil-C18 Silicagel column (15 cm×16 mm, with 5 μm diameter particle size silica) with a 40/60 water/acetonitrile eluent mixture was used for separation. The detector wavelength was 254 nm. The identity of the intermediates as well as of residual CB was confirmed by comparing retention times with those of known standards, and their concentrations determined from calibration curves. The chlorobenzene conversion was determined by differences between initial (C_i) and residual CB (C_f) concentration according to formula: $Conv = 100*(C_i - C_f)/C_i$.

3 Results

The CB's sonolysis intermediates were identified by HPLC-MS analysis of crude reaction mixture and are shown in the Scheme 1. Their concentrations (in μmoles) for each metal chloride salt employed are given in Tables 1-4.



Scheme 1 Reaction products identified in CB's sono-degradation.

3.1 Sonolysis of aqueous CB in the presence of PdCl₂

The products distribution for different sonication time of CB/water solution in the presence of palladium chloride is reported in Table 1.

As is evident from Table 1, in the presence of smaller concentration of PdCl₂, after short sonication for 10 min the CB's conversion is rather low. Phenol 8 is the main reaction product along with trihydroxyphenols 1, 2 and 3. When using 0.90 mM salt concentration, the conversion at short sonication time was significantly higher otherwise the distribution of products was similar to the previous experiment.

3.2 Sonolysis of aqueous CB in the presence of FeCl₂ and FeCl₃

The products partition for CB/water solution sonolysis in the presence of iron chlorides are given in Tables 2 and 3.

When using FeCl₂ or FeCl₃, benzene 12 was identified in the early stages of sonication. Phenol 8 appeared in higher amounts than before and significant quantities of chlorophenols were also detected.

3.3 Sonolysis of aqueous CB in the presence of CoCl₂

Sonolysis of CB/water solution in the presence of cobalt (II) chloride gave the products presented in Table 4.

As in the case of palladium chloride, benzene was never detected in the presence of cobalt chloride but chloro-phenols were formed in large amounts. Phenol 8 was also present as one of the major products of CB sonolysis.

The results of sonolysis of CB/water solution are reported in the Table 5.

Even in the absence of any salt, the conversion of CB is high. Surprisingly, the amount of benzene was significant at the beginning, which vanished at 30 minutes and reappeared at 60 minutes.

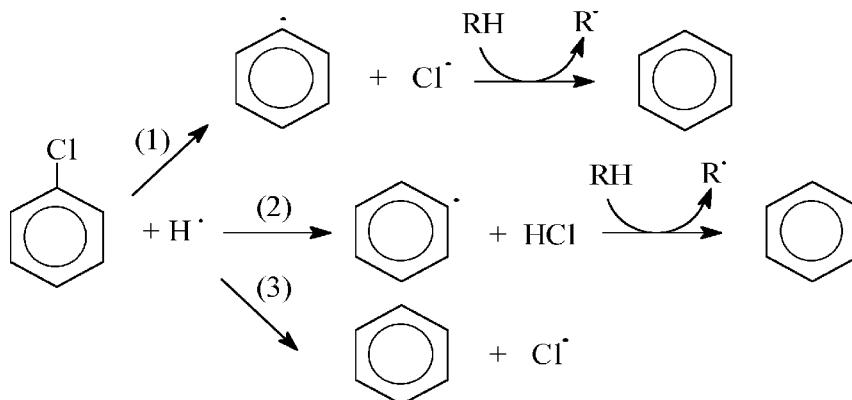
4 Discussions

From the data shown in tables 1-5, benzene 12, phenol 8, poly-phenols and chloro-phenols are the most important products detected in the aqueous solution. It is of interest to determine if these products are formed in parallel or by consecutive reactions and which one is the intermediate, in order to elucidate the CB sono-degradation mechanism.

4.1 Benzene formation

As can be seen in the Scheme 1, benzene 12 is one of the products issuing from CB sono-decomposition. Benzene was found in the experiments performed in the absence of any salt and in the presence of iron chlorides and was lacking when Pd and Co chlorides were

added. In previous papers, we reported similar effects when sulfate salts were employed. We pointed out that benzene is the main intermediate of CB sonolysis [16]. Three different pathways for benzene formation are proposed in the literature (Scheme 2) [18].



Scheme 2 Proposed mechanisms for benzene formation.

Examining this scheme, it is obvious that first pathway takes into account the CB decomposition inside cavitation. The resulting phenyl radicals could react inside cavitation with H and HO radicals to give benzene or phenol or can migrate into the bulk solution to react there with the solvent, in this case water, leading to benzene and HO radicals. If benzene is formed by this mechanism it should be present as a product/intermediate regardless of the addition of metal salt. However, when palladium or cobalt salt or even high concentration of ferric chloride were added benzene was totally absent pointing to the fact that this mechanism is not the prevailing one or has a minor contribution to benzene generation.

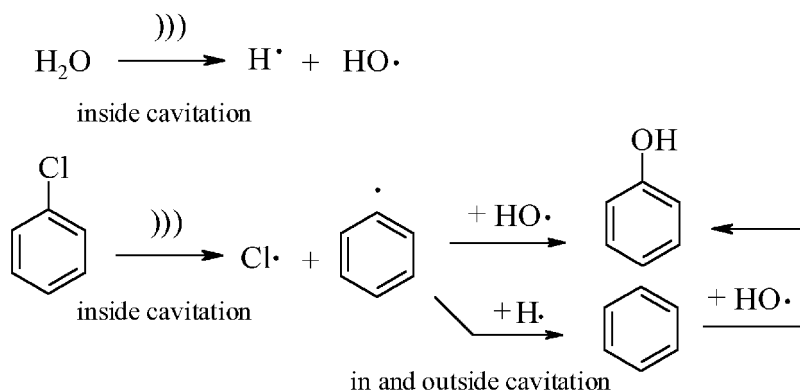
The second pathway, halogen abstraction by hydrogen atoms directly from CB, is rather of minor importance for the same reasons as above.

In the third pathway, benzene is formed by direct substitution of chlorine atom by hydrogen, a reaction that should take place only inside cavitation where hydrogen atoms are hot enough to produce this reaction. In this case also benzene should be present regardless of the reaction conditions or additives, but the fact that Pd and Co salts stopped the benzene formation pleads against this mechanism.

Knowing that palladium salts undergo reduction to metal under ultrasonic irradiation in a bulk reaction [19], and that benzene formation is not observed when palladium salts were added, it is reasonable to assume that palladium is reduced at the expense of hydrogen atoms that, otherwise, are used for benzene formation.

One may conclude that benzene is the key intermediate of CB sono-degradation and its main formation pathway is an outside cavitation reaction of phenyl radicals with hydrogen atoms that escaped from collapsing bubbles (Scheme 3). We cannot totally exclude the generation of benzene inside cavitation, but this reaction seems to be of

minor importance for CB sono-degradation mechanism.

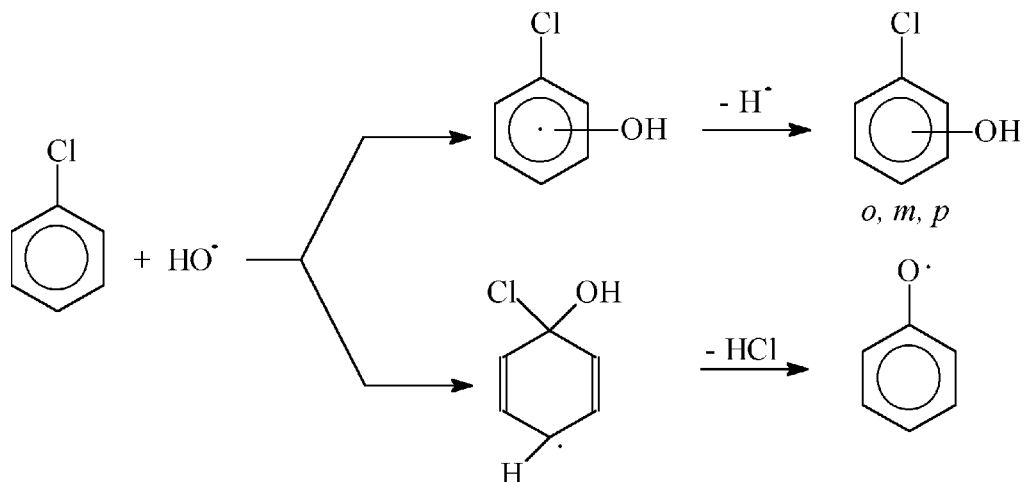


Scheme 3 Primary reaction in CB's sono-decomposition.

4.2 Phenol formation

After establishing benzene as key intermediate in CB sono-degradation, it was important to find the origin of phenol. As shown in scheme 3, phenol could be a product of in/out cavitation reaction.

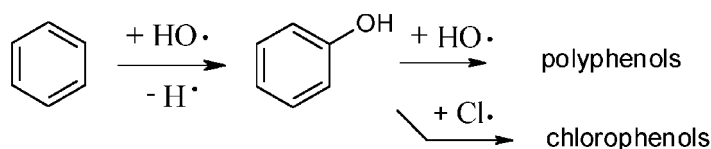
In literature, the production of phenol and chloro-phenols is explained by several mechanisms (Scheme 4) [20, 21].



Scheme 4 Proposed mechanisms for formation of phenol and chloro-phenols.

If either of this mechanism operates, then regardless of the presence or absence of metal salts, phenol and chloro-phenols should be formed in large amounts. Thus, assuming that Pd (II) reacts with hydrogen atoms in bulk solution, the amount of HO radicals should be high and the probability of attack of HO radicals on CB should be accordingly high. However, we found the chlorophenols in deceptively small amounts when using palladium chloride. Most probably, chloro-phenols issued from the reaction of phenol with chlorine atoms, a reaction that takes place very fast [22].

It is possible that some phenol is formed inside cavitation by combination of phenyl and HO radicals, but the phenol is mainly an outcome from reaction of benzene with excess HO radicals in bulk solution (Scheme 5).



Scheme 5 Mechanism of benzene reactions outside cavitation.

Phenol is a very reactive compound towards radicals [23], explaining thereby the formation of polyphenols observed experimentally.

Due to extreme conditions arising from the collapse of bubbles, a part of CB and intermediate products of its sonolysis ultimately undergo deeper decomposition leading to gaseous products like acetylene, methane, CO, etc., [7].

4.3 The role of metal salt and chloride anion

The CB undergoes sono-decomposition even in the absence of metal salts, therefore the question arises as to the advantages of adding salts in this type of decomposition. The wastewater effluents contain a number of toxic elements, including metals, because under practical conditions wastes from many industrial sites are discharged directly. In the present study we tried to simulate conditions that are close to those found in reality. These experiments brought to light new information on the chemistry involved in CB's sono-decomposition.

Comparing the sonication experiments in the presence and absence of metal salts, we observed that phenol was present in minor amounts in the latter than in the former. In case of benzene, it was present in experiments conducted in absence of salts and totally absent in experiments carried out with Pd, Co and Fe (III).

According to the nature of metal, some of them suffer oxido-reduction during sonolysis; others undergo reduction to the zero valence metal. Both reaction types occur in bulk solution prompting us to discriminate between inside and outside (bulk solution)

reactions.

The palladium chloride undergoes reduction of the ionic metal to zero valence metal, a reaction that takes place in bulk solution [19]. Its reduction is at the expense of hydrogen atoms generated from sonolysis of water. Thus, only small amounts of hydrogen are available for reduction of phenyl radical to benzene and this explains the absence of benzene in the experiments with palladium salt. As soon as benzene is formed, it reacts very fast with excess HO radicals to give phenol, which explains the formation of larger amounts of phenol at the beginning of reaction. As the reaction advances, the phenol quantity rises. Palladium reduction produces protons that act as counter ions for chloride anions, diminishing the available chlorine atoms to give chlorophenols. It explains the fact that small amounts of chlorophenols were detected in this experiment.

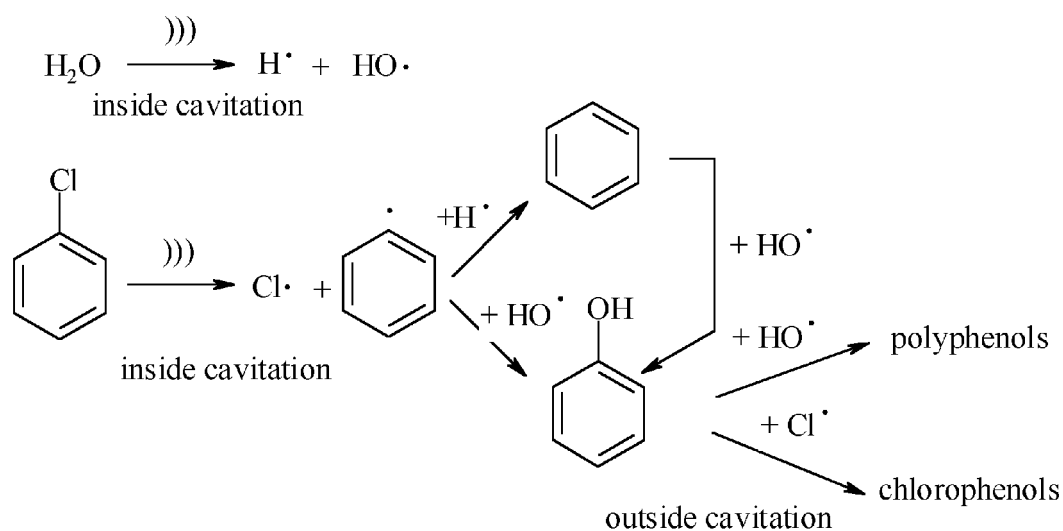
The amount of chlorophenols formed in the case of cobalt is in-between palladium and iron. This may be explained as follows: water sonolysis leads to formation of high amounts of hydrogen peroxide. In the reaction mixture in the presence of hydrogen peroxide and chlorine Co(II) is oxidized to Co(III) [24]. By this reaction some amounts of hydroxyl radicals are released and thus phenol is formed. In water solution Co(III) is not stable and as soon as is formed is reduced back to Co(II). By this reaction some chlorine is released into the bulk solution where it reacts with phenol leading to chlorophenols. This behavior situates cobalt in the middle among palladium and iron chlorides.

Fe (II) oxidation occurs at the expense of HO radicals, leaving hydrogen atoms that consume chlorine atoms to give hydrochloric acid. In this way less chlorine remains for chlorophenol formation. On the contrary, Fe (III) reduction occurs at the expense of hydrogen atoms and excess HO radicals give more phenol and therefore more chlorophenols are formed.

The large amount of phenol found during the sonication with added metal salts may also be due to its complexation with metals. This subject is under investigation and will be the matter of forthcoming publication.

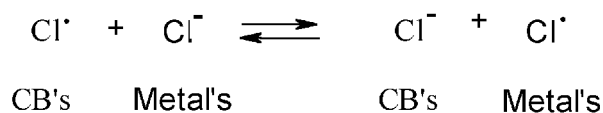
As was proposed in scheme 5, chlorophenols result from phenol reaction with chlorine atoms. This mechanism pleads against possible formation of chlorophenols from the reaction of chlorine anion with an intermediate of CB sono-decomposition. There is no evidence that during CB's sono-decomposition a cationic intermediate able to react with chlorine anion is possibly formed.

In the experiment without addition of any salt, the chlorine anions are absent hence all chlorophenols would be coming only from chlorobenzene. Since there is no significant difference between the experiments with salts with respect to the formation of chlorophenol it is reasonable to conclude that the chlorophenols are not formed from chlorine anions. CB's sono-degradation has a unique mechanism, regardless the presence or absence of metal salts (Scheme 6).



Scheme 6 Sono-degradation mechanism of chlorobenzene.

However, we cannot totally exclude the scrambling of chlorine via electron transfer as illustrated in scheme 5.



Scheme 5

Conclusions

The ultrasonic irradiation in the presence of Fe (II) and Fe (III) ions leads to an increased amount of phenolic-type products, with no visible change in the CB degradation rate. Chlorophenols are formed in high amounts at the beginning of the sonication and are degraded during reaction, indicating the fact that they are only intermediates. The efficiency of Pd (II) was significant: a low amount of chlorophenols and phenolic products was detected.

It was found that palladium might be a useful tool in determining the sonochemical decomposition mechanism and reaction site of noxious compounds.

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Products	0.45 mM PdCl ₂			0.90 mM PdCl ₂		
	10 min	30 min	60 min	10 min	30 min	60 min
1	8.6	16.2	8	5.7	15.6	24
2+3	37.8	73	94	51.7	90.5	135
4	-	-	-	-	-	-
5	-	31	43	-	-	-
6	5.8	16.8	31	8.5	18.6	31
7	-	1	-	10.3	1.2	-
8	87.8	209	369	99.5	185	224
9	-	29.2	27	18.6	31.9	36
10	-	-	-	-	-	-
11	-	-	-	-	-	-
12	-	-	-	-	-	-
CB conversion %	35.7	74.3	100	63.9	88.1	100

Table 1 Distribution of the reaction products in $\mu\text{M}/\text{l}$, for PdCl₂.

Products	0.45 mM FeCl ₂			0.90 mM FeCl ₂		
	10 min	30 min	60 min	10 min	30 min	60 min
1	6.1	7	13	8	6	15
2+3	72.4	192	228	75	134	362
4	-	37	35	35	56	38
5	85.7	71	72	77	67	55
6	5.6	11	15	2	7	10
7	6.6	13	9	10	19	19
8	137.7	183	245	95	134	129
9	30.8	55	64	42	83	122
10	50	89	16	131	154	16
11	47.5	50	15	93	81	24
12	47	-	-	71	37	-
CB conversion %	55.7	78.9	85.7	64.9	79.5	100

Table 2 Distribution of the reaction products in $\mu\text{M/l}$, for FeCl₂.

Products	0.45 mM FeCl ₃			0.90 mM FeCl ₃		
	10 min	30 min	60 min	10 min	30 min	60 min
1	7	15	20	9	10	11
2+3	36	120	219	46	80	191
4	-	-	-	-	-	18
5	124	125	128	37	32	27
6	4	7	9	6	11	19
7	8	16	17	8	13	12
8	73	83	97	106	165	263
9	34	71	91	40	66	45
10	111	126	65	100	107	25
11	69	57	41	67	40	16
12	57	53	-	-	-	-
CB conversion %	57.3	75.8	88.3	59.3	75.0	90.9

Table 3 Distribution of the reaction products in $\mu\text{M/l}$, for FeCl₃.

Products	0.45 mM CoCl ₂			0.90 mM CoCl ₂		
	10 min	30 min	60 min	10 min	30 min	60 min
1	8.8	8.6	9.8	9.4	12	16.5
2+3	80.2	57.2	197.2	81.8	104.4	153.7
4	-	22.5	-	-	-	-
5	80.2	126	93.3	144.6	98.6	102
6	3.8	6.8	10.2	4.4	5.7	8.3
7	9.6	16.4	18.1	8.6	14.9	18.4
8	97.5	125	195.6	88	121.6	165.2
9	-	48.2	58.7	-	40.2	50.5
10	99.1	100.9	67.7	106.9	142.2	109
11	59.7	67.7	7.4	56.6	66	9.4
12	-	-	-	-	-	-
CB conversion %	61.1	77.7	86.8	68.4	86.0	89.0

Table 4 Distribution of the reaction products for CoCl₂ ($\mu\text{M}/\text{l}$).

Products	10 min	30 min	60 min
1	5.8	11.8	16.6
2+3	19.3	65.1	144.9
4	-	-	-
5	-	-	-
6	0.7	1.9	3.0
7	6.6	11.2	12.5
8	27.7	17.9	47.7
9	18.3	39.3	48.5
10	94.1	101.4	23.2
11	76.3	48.5	12.3
12	156.1	-	118
CB conversion %	55.6	77.4	98.7

Table 5 No additives

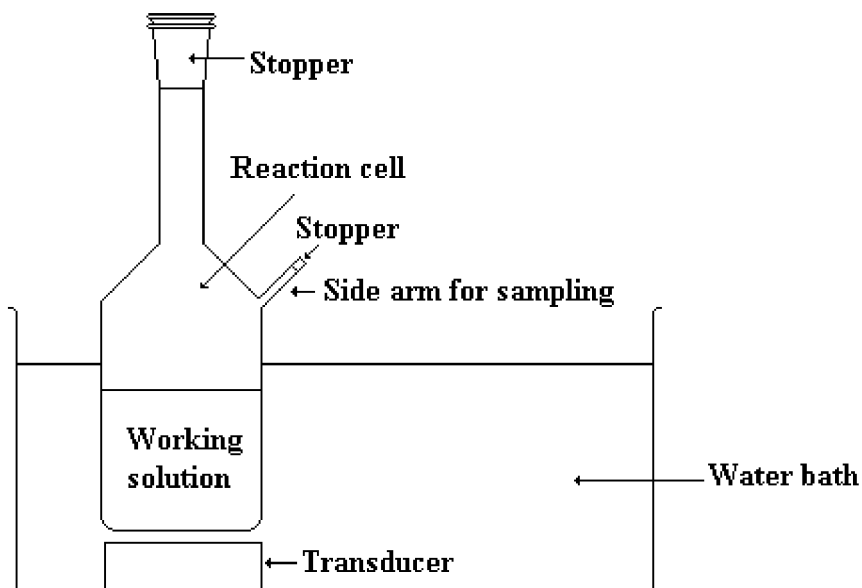


Fig. 1 Experimental setup for CB's sono-degradation studies.