SONOCHEMICAL ELIMINATION OF METHOXYLATED AROMATIC POLLUTANTS

E. Combet+, C. Pétrier+, O. Devos+, M. Barbe+, J.-L. Ravanat#, and T. Lepoint*
+Laboratoire Chimie Moléculaire et Environnement, Université de Savoie, Le Bourget du Lac, France
Laboratoire Lésion des Acides Nucléiques, DRFMC/SCIB, CEA Grenoble, France
* Institut Meurice, Bruxelles, Belgique
Christian.Petrier@univ-savoie.fr

Abstract

Methoxylated aromatic compounds are important contaminants of natural and waste waters that have to be removed in water treatment processes. Ultrasonic application was found efficient in the elimination of several model compounds: anisole, 4-hydroxyanisole, 4-methylanisole.

Elimination yields and behaviour depend on the gas/water partition of the target molecule.

Comparison of the reaction rates at 300 kHz, 600 kHz, 800 kHz exhibits a frequency dependence with a better yield at 300 kHz. The connection between reaction rate and frequency of the wave appears linked to the hydrogen peroxide formation.

Products found in the case of sonochemical treatment of anisole evidence a simultaneous transformation through reactions with HO° radicals and thermolysis in supercritical conditions. Formation of aldehyde, naphthalene and fluorene, suggests high temperature rearrangement of the aryl methyl ether bond.

Introduction

Aromatic compounds are important contaminants of natural and waste waters. Most of these aromatics, characterised by methoxyl substituents, are natural humic substances or issued from industrial wood transformation [1]. By reaction with chlorine, these aromatics are involved in the formation of harmful chloroforme and trihalomethanes [2]. Therefore they have to be removed prior the disinfection step of water.

Previous works have demonstrated that ultrasonic treatment alone or in combined processes is able to eliminate from water such undesirable compounds.

Products and intermediates of the sonochemical elimination of anisole and derivatives have not yet been found out. In this work, in order to get more information on the sonochemical action, the behaviour of this class of molecules at different ultrasonic frequencies is investigated.

Material and Methods

Reactions were performed at 21°C +/-1°C in a cylindrical jacketed glass cell previously described [3].

The ultrasonic waves were emitted from ceramic titanate-lead zirconate disk transducers (diameter 4 cm Quartz et Silice P 7/69) fixed on a pyrex disk (diameter 5 cm) having a thickness of half a wavelength. Transducers were driven by a high-frequency power supply (ULV 300A) from Radiocoms Systemes.

The ultrasonic power dissipated into the reactor was estimated through the calorimetric method.

Reactions were carried out in deionised water (300 mL) saturated with dioxygen or argon.

Progress of the reaction was monitored by periodical withdrawal. Quantitative analysis and identification of starting compounds and products were performed by HPLC and GC-MS methods.

Hydrogen peroxide concentration has been determined iodometrically.

Results

Yields of anisole degradation.

As usually observed in the case of aromatic compounds [4], sonochemical treatment in the high frequency range of anisole in aqueous solution (10^{-3} mol L^{-1}) exhibits an exponential decrease of the initial concentration with sonication time (Figure 1).

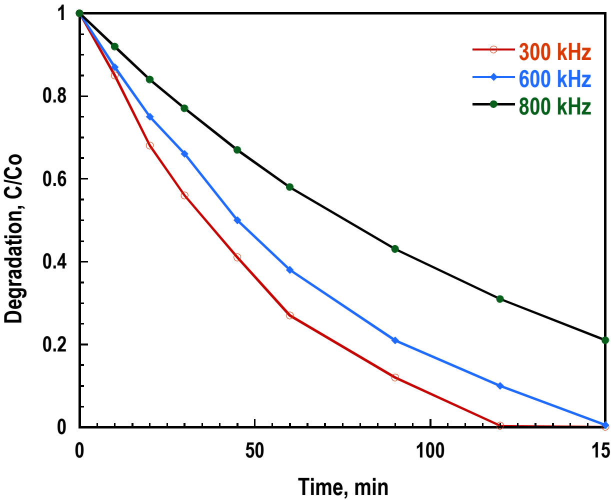


Figure 1: Anisole concentration versus sonication time. 300 mL oxygen saturated solution. P_w = 36 W based upon calorimetric method.

Comparison of the sonochemical efficiency at different frequencies can be done following different methods of calibration [5]: (i) input electric power, (ii) calorimetric method, (iii) chemical dosimetry.

Calibration at each of the three frequencies, using the calorimetric method which gives an indication on the ultrasonic power dissipated into the solution, points out a frequency effect. For the same ultrasonic power applied (36 W), better yield is obtained for the lower frequency used. The electric input at the transducer was 60 W in the 300 and 600 kHz experiments; it was set at 100 W for the 800 kHz experiment.

This better yield observed at 300 kHz can be connected with hydrogen peroxide formation rate which is exalted at this frequency (Table 1).

Table 1: Initial rate of anisole degradation and hydrogen peroxide rate of formation in absence of solute (300 mL of water saturated with oxygen. $P_{calorimetry} = 36W$).

	H_2O_2 Rate of formation	Anisole Initial degradation rate
300 kHz	1.53 µmol min^{-1}	4.23 µmol min^{-1}
600 kHz	0.69 µmol min^{-1}	3.37 µmol min^{-1}
800 kHz	0.37 µmol min^{-1}	2.2 µmol min^{-1}

Hydrogen peroxide comes from the activity of the bubble of cavitation generated by the periodical change of the pressure in the acoustical field. Pulsation and collapse of the bubble conduct to high energy states (temperature and pressure) that can dissociate water and molecular oxygen.

- $H_2O \rightarrow H + HO$
- $O_2 \rightarrow 2\ O$

These reactive species combine in different ways in the bubble

- $H + O_2 \rightarrow HOO$
- $O + H_2O \rightarrow 2\ HO$
- $H + HO \rightarrow H_2O$

Hydrogen peroxide results from radical combination at the cooler interface of the bubble [6-7].

- $2\ HOO \rightarrow H_2O_2 + O_2$
- $2\ HO \rightarrow H_2O_2$

In the ultrasonic conditions, degradation of an organic contaminant can occur in different ways conducting to the formation of specific products:

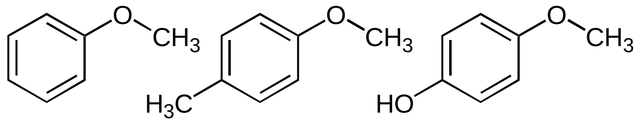
-an hydrophilic molecule will react at the interface of the bubble with hydroxyl radicals, competing with the reaction engendering hydrogen peroxide. In this case, hydroxylated products are detected in the first time of the treatment.

-a molecule with high fugacity character in water will enter into the bubble and will be thermally decomposed, conducting mainly to soot and gaseous products (CO, CO_2, CH_4, C_2H_2) [4,8].

-it has also been assumed that some reactions would occur in a layer of supercritical water surrounding the gas bubble [9].

Degradation of substituted anisoles.

Comparison of the degradation rates of substituted anisoles (4-hydroxyanisole, 4-methylanisole) demonstrates that the sonochemical rates depend on the fugacity character of the molecule rather than on the HO rate constant.



Anisole **4-Methylanisole** **4-Hydroxyanisole**

Anisole and 4-methylanisole, the compounds having the same higher value of the Henry's law, constant will degrade at a faster rate than 4-hydroxyanisole. 4-Hydroxyanisole has a higher value of the HO rate constant than anisole but a lower value of the Henry's law constant (Figure 1, Table 2).

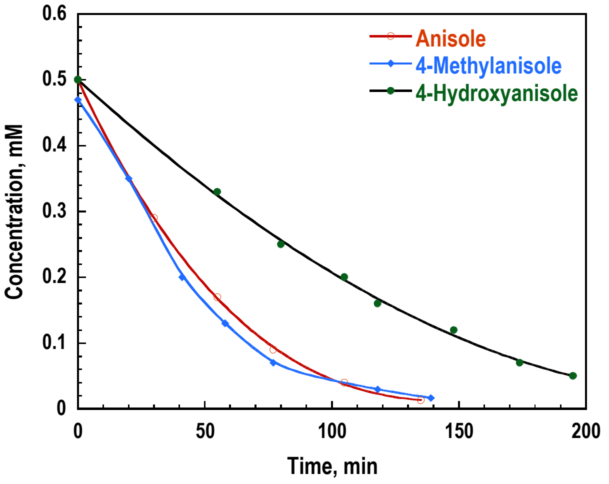


Figure 2: Time course degradation at 600 kHz of anisole and substituted anisoles. 300 mL oxygen saturated solution. $P_w = 40$ W based upon calorimetric method.

Table 2: Physical properties at 25°C and HO rate constant of anisole and substituted anisole. Ws: Water solubility, mg L^{-1}; Vp: Vapor pressure, mm Hg; HL: Henry's law constant, atm m^3 mol^{-1}; k_{HO}: Rate constant for HO in aqueous solution, L mol^{-1} s^{-1} [10-11].

	Ws	Vp	HL	k_{HO}
Anisole	2.53 10^3	3.54	4.35 10^{-3}	5.4 10^9
4-Methylanisole	6.7 10^2	1.14	4.66 10^{-3}	
4-Hydroxyanisole	4 10^4	8.3 10^{-3}	5.53 10^{-7}	2.6 10^{10}

Products of anisole sonochemical degradation.

In order to localize the place where sonochemical reaction occurs, a detailed investigation on the products of the reaction was undertaken. Products formed were compared with those obtained from gamma radiolysis experiment.

In the gamma radiolysis experiment, for an anisole aqueous solution saturated with oxygen, only the three products expected from hydroxyl radical reaction were formed: 4-hydroxyanisole, 2-hydroxyanisole, phenol.
In the case of the sonochemical treatment under oxygen, these hydroxylated products were detected along with products resulting from HO addition and cleavage or rearrangement of the ether bond: hydroquinone, catechol, benzaldehyde (Figure 3).

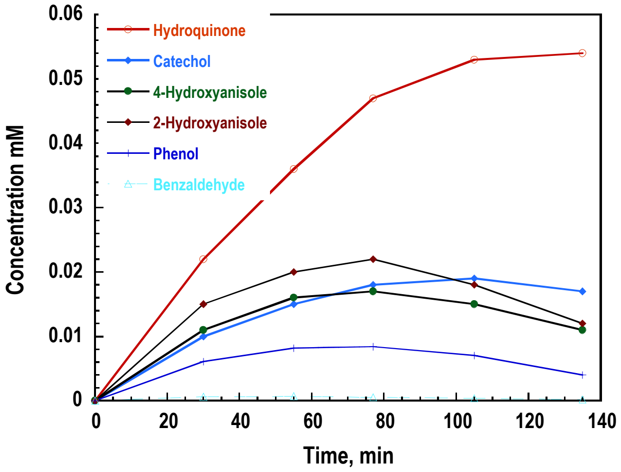
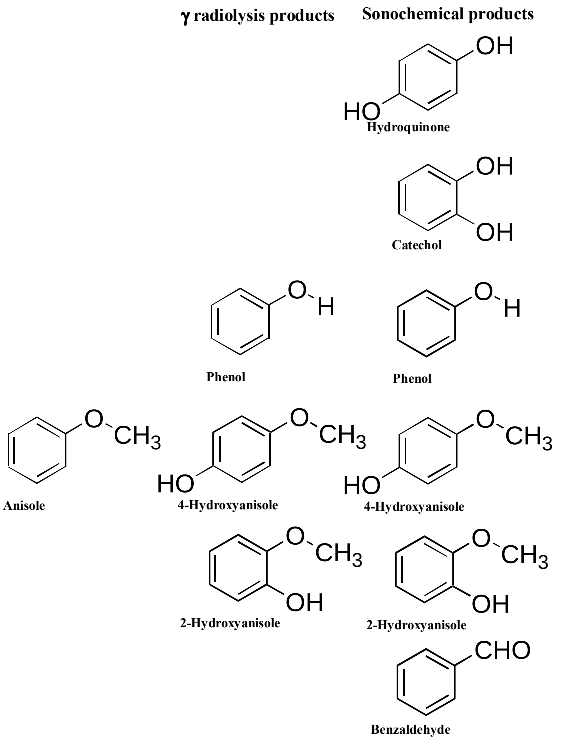


Figure 3: Products of Anisole (5 10^{-4} mol L^{-1}) degradation versus sonication time (HPLC analysis). 300 mL oxygen saturated solution. 600 kHz, $P_w = 40$ W based upon calorimetric method.

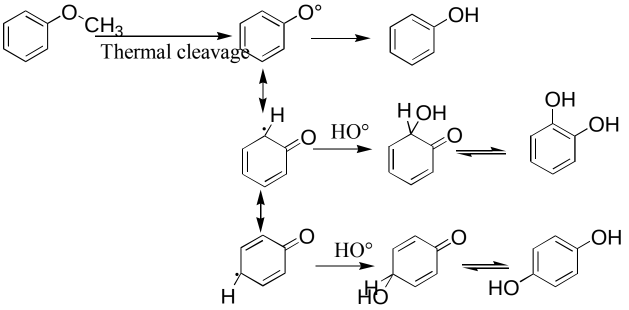


Due to the strong ortho-para directing effect of the methoxy group in anisole, the hydroxyl radical addition conducts mainly to 4 and 2-hydroxyanisole with some phenol resulting from addition at the α position [12].
Furthermore, under ultrasound, the phenol can be also formed by cleavage of the aryl-O-CH_3 bond that can occur through thermolysis of the weak methyl ether bond (61 Kcal mol^{-1}) or through nucleophilic water addition in supercritical water[13-14].

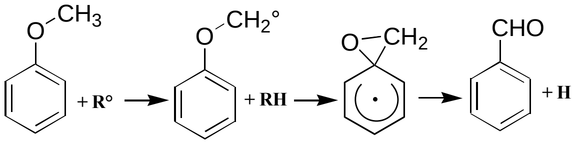
$$C_6H_5\text{-}O\text{-}CH_3 \rightarrow C_6H_5\text{-}O^\circ + CH_3^\circ$$
$$C_6H_5\text{-}O^\circ + H \rightarrow C_6H_5OH$$

$$C_6H_5\text{-}O\text{-}CH_3 + H_2O \rightarrow C_6H_5OH + CH_3OH$$

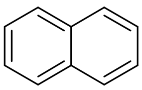
Hydroquinone and catechol, which were not observed with gamma radiolysis, were produced simultaneously with 2- and 4-hydroxyanisole under ultrasound. These compounds could be formed by HO addition to the phenoxy radical as follows:

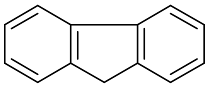


Aldehydes are products usually found in thermal treatment of aryl methyl ethers [15]. The reaction involves the formation of a spiranic oxirane which rearranges.

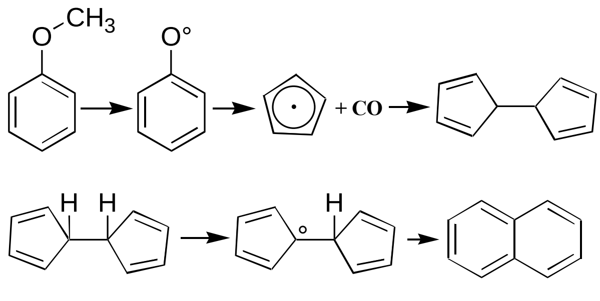


When the sonochemical treatment is conducted under argon atmosphere, phenol comes out as the main product of the reaction with the formation of poly aromatic hydrocarbons (PAHs): fluorene and naphthalene.
These two last molecules are known as products of anisole pyrolysis.


Naphthalene


Fluorene

Naphthalene implies the formation of cyclopentadienyl radicals that combine to generate 9,10-dihydrofulvalene. Hydrogen abstraction engenders the hydrofulvalenyl radical that rearranges into naphthalene [16].



Conclusion

This preliminary study on the behaviour of anisole and substituted anisoles under sonication in water shows complex and simultaneous reactions connected with hydroxyl radical chemistry, supercritical conditions and thermal chemistry.

Additional analytical information (eg.gaseous compounds) is required to have a clear and complete understanding of the anisole degradation mechanism.

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