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Sono-bromination of aromatic compounds based on the ultrasonic advanced oxidation processes



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1. Introduction

Brominated aromatic compounds are widely used as precursors and products in the synthesis of pharmaceutical and agricultural chemicals [1,2] and play vital roles in metal catalyzed coupling reactions [3–5]. The most conventional brominating agent remains topically Br₂, although it is hazardous and difficult in handling together with poor atom efficiency. A large panel of brominating reagents have been thus developed, including molecular bromine with or without catalysts [6-9], N-bromosuccinimide (NBS) 1,3-dibromodimethylhydantoin (DBDMH) [13,14], [10–13], N,N-dibromo-p-toluenesulfonamide (TsNBr₂) [15], KBrO₃ [16], or quaternary ammonium tribromide [17–19], etc. All of the aforementioned reagents are used in stoichiometry amount, more or less efficient, expensive, toxic, not commercially available and lead to large amounts of wastes at the end of the reaction. To overcome or at least to limit these negative impacts, some researchers have developed several combinations involving hydrobromic acid or alkaline metal bromide with suitable oxidants such as hydrogen peroxide [20-22], tert-butylhydroperoxide [23], peroxymonosulfate (oxone) [24], peroxodisulfate [25], bromate [26], DMSO [27,28], or hot conc. H_2SO_4 [29] to produce *in situ* the desired brominating agent starting from harmless reagents. In reason of

ABSTRACT

A novel, mild "sono-halogenation" of various aromatic compounds with potassium halide was investigated under ultrasound in a biphasic carbon tetrachloride/water medium. The feasibility study was first undertaken with the potassium bromide and then extended to chloride and iodide analogues. This methodology could be considered as a new expansion of the ultrasonic advanced oxidation processes (UAOPs) into a synthetic aspect as the developed methodology is linked to the sonolytic disappearance of carbon tetrachloride. Advantages of the present method are not only that the manipulation of the bromination is simple and green, but also that the halogenating agents used are readily available, inexpensive, and easy-handling.

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the crucial requirement for our society to develop more sustainable organic synthetic chemistry routes to limit the environmental impact, further developments towards a greener brominating method of organic molecules are highly desired.

The birth of the Green Chemistry concept strongly contributed to the recent renaissance of sonochemistry. Indeed, ultrasound is recognized not as an "exotic" non conventional activation method, but more as an important tool to Green Chemistry able to attract more and more researchers looking for innovative, simple, quick and efficient activation methods. In the last decade, a lot of applications have been subsequently found in inorganic, organometallic and organic synthesis, in both homogeneous and heterogeneous catalysis, in polymer chemistry or in biomedical pharmaceuticals [30]. It has been reported that ultrasound facilitates ring bromination using NBS in an acetic acid [31] or in water [35], with *p*-toluenesulfonic acid (TsOH) [32,33] or with acid catalyst Amberlyst [34].

Herein, we report a novel "sono-bromination" of aromatic compounds with simple alkaline metal bromide associated with the advanced oxidation process [36-39] by ultrasound. The advantages of the present method are that the manipulation of the reaction is simple and reagents used are readily available, inexpensive, easy-handling, and environmentally friendly apart from carbon tetrachloride. CCl₄ suffers rapid decomposition in an aqueous medium and generates intermediate radical species which lead to the *in situ* formation of brominating species.



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2. Experimental

2.1. General procedures

All chemicals are commercially available and used as received. Bath type sonochemical reactors having a 36.6 or 480 kHz frequency (Honda electrics, Japan) were used The temperature of the bath was maintained at 20 ± 2 °C by circulating thermo-controlled water and the water level inside the bath was kept constant. Power of ultrasound introduced into a reaction vessel was measured by calorimetrically [40,41] and was adjusted to 5 W unless otherwise noted. Yields, conversions, and selectivity's were determined by GC (Shimadzu GC-14A). Products were identified by comparison with authentic standards using GC, NMR (JEOL JNM-GX270), and GC–MS (Shimadzu GCMS-QP5050A).

2.2. General procedure of sono-bromination of anisole

In a cylindrical reaction flask with a flat bottom, 0.1 mmol of anisole and 0.15 mmol of KBr were dissolved in a mixture of 5 mL H_2O and 1 mL CCl₄. Then the biphasic solution was submitted to ultrasound in a 36.6 or 480 kHz thermo-controlled ultrasonic bath for 1 h at 20 °C. Silent runs under harsh mechanical stirring at 1400 rpm were also carried out for comparison. Organic materials were separated into CCl₄ phase and analyzed by GC using the internal standard method. Evaporation of the solvent under reduced pressure yielded crude product, which was almost pure monobromoanisole.



3. Results and discussion

Sono-bromination with KBr was conducted in H_2O in the absence and presence of CCl₄, and in CCl₄ alone. The study of this reaction in several solvent systems brought out the importance of both water and CCl₄ as both were found to be necessary for the sono-bromination. Indeed, when CCl₄ was absent, only decomposition of anisole occurred (entry 1, Table 1) whereas when a little quantity of CCl₄ was used, monobromoanisole as well as dibromoanisole in a lesser extent were obtained avoiding the decomposition of anisole (entries 2 and 3, Table 1). There is no doubt that

| Table 1 | | | | |
|--------------|------------------------|--------|----------|------------------------|
| The effect o | of CCl ₄ or | yields | of brome | oanisole. ^a |

| Entry | CCl ₄ (mL, mmol) | | Anisole recovered (%) ^b | Bromo anisole (%) (2-:4-) ^b | Dibromoanisole (%) ^b |
|----------------|--------------------------------|------|---------------------------------------|---|------------------------------------|
| 1 | 0.00 | 0.0 | 21 | 0 | 0 |
| 2 | 0.25 | 2.57 | 0.4 | 72 (6:94) | 16 |
| 3 | 0.50 | 5.15 | 0 | 85 (9:91) | 12 |
| 4 | 1.00 | 10.3 | 0 | 99 (3:97) | 0 |
| 5 [°] | 1.00 | 10.3 | 0 | 0 | 0 |
| 6 ^d | 5.00 | 51.4 | 100 | 0 | 0 |

 a Anisole (0.1 mmol), KBr (0.15 mmol), $H_{2}O$ (5 mL), time (1 h), ultrasound (480 kHz, 5 W).

^b GC analysis.

^c Mechanical stirring (1400 rpm).

 $^{\rm d}$ Anisole (0.1 mmol), KBr (0.15 mmol), CCl4 (5 mL), time (1 h), ultrasound (480 kHz, 5 W).

the reaction occurs by ultrasonic irradiation because under harsh mechanical stirring conditions, bromination did not take place at all (entry 5, Table 1).

Additionally, the amount of added CCl₄ also seems to exert a certain influence on the amount of brominated species. A gradual increase of added CCl₄ leads to a gradual disappearance of dibromoanisole in favor of monobromoanisole. Under a CCl_4/H_2O ratio 1/0, the bromination was not observed at all. This observation has certainly to be taken into account to reveal the whole mechanism.

The effect of the amount of KBr on the reaction was then explored and results are summarized in Table 2. In the absence of KBr, mono- and di-chlorination occurred in 49% and 22% yields, respectively under ultrasonic conditions (entry 1, Table 2). The increased amount of KBr seems to mechanistically exert a similar effect to the previously studied parameter (increasing amount of CCl₄). Indeed, a gradual increase of added KBr leads also to a gradual disappearance of the chlorinated species in favor of their brominated homologues. Moreover, when KBr was present at 1.5 M excess of anisole, only monobromoanisole was obtained in 99% yield (entry 4, Table 2). We certainly face competitive pathways originating from the sonolytic decomposition of CCl₄ with an apparent priority of bromination over chlorination.

As previously stated, the presence of CCl_4 is essential for the sono-bromination (entry 1, Table 1). The ultrasonic degradation of aqueous solutions of CCl_4 has been intensively studied during the 90s. Several mechanisms were then proposed, including the followings [42–45]:

$$CCl_4 \xrightarrow{)))} \cdot CCl_3 + \cdot Cl$$
$$\cdot Cl + CCl_4 \xrightarrow{)))} Cl_2 + \cdot CCl_3$$
$$\cdot Cl + \cdot Cl \xrightarrow{)))} Cl_2$$
$$Cl_2 + H_2O \rightarrow HClO + HCl$$

 $\cdot OH + CCl_4 \rightarrow HClO + \cdot CCl_3.$

In the absence of KBr, the generated 'Cl, Cl₂, or HClO species are probably responsible for the sono-chlorination of anisole (entry 1, Table 2). When KBr was added, however, bromoanisole was obtained (Table 2). Bromide ion has thus to be oxidized to be eligible to react for the aromatic substitution. Which species can then oxidize Br⁻? The irradiation of ultrasound onto water results in the pyrolysis of water, producing 'OH and 'H radicals [46]. The formed 'OH radical can thus oxidize Br⁻ in a similar manner to Weissler reaction [47,48]. As bromination of anisole in the

| Table 2 |
|--|
| The effect of KBr on yields of bromoanisole and chloroanisole. |
| |

| Entry | KBr (mmol) | Anisole recovered (%) ^b | Bromoanisole (%) (2-:4-) ^b | Chloroanisole (%) (2-:4-) ^b |
|----------------|---------------|---------------------------------------|--|---|
| 1 | 0.00 | 19 | - | 49 (30:70) ^c |
| 2 | 0.05 | 24 | 30 (10:90) | 37 (24:76) |
| 3 | 0.12 | 0 | 73 (10:90) | 14 (10:90) |
| 4 | 0.15 | 0 | 99 (3:97) | 0 |
| 5 | 0.20 | 0 | 94 (5:95) | 0 |
| 6 ^d | 0.15 | 85 | 3 (0:100) | 0 |

 $^{\rm a}$ Anisole (0.1 mmol), CCl_4 (1 mL), H_2O (5 mL), time (1 h), ultrasound (480 kHz, 5 W).

^b GC analysis.

^c Dichloroanisole was a byproduct at 22% yield.

^d As a radical quenching experiment, *t*-BuOH (0.1 mL,1.05 mmol) was added.

presence of KBr takes place rather than decomposition of anisole, the 'OH seems to attack Br⁻ rather than an aromatic ring directly as follows:

$$H_2O \xrightarrow{)))} OH + H$$

 ${}^{\boldsymbol{\cdot}}OH+Br^{-}\rightarrow OH^{-}+{}^{\boldsymbol{\cdot}}Br$

 ${}^{\bullet}OH + {}^{\bullet}Br \to HBrO$

$$Br + Br \rightarrow Br_2$$

The second order rate constants of the reaction of 'OH with Cl⁻, Br⁻, and l⁻ were reported 4.3×10^9 , 1.1×10^{10} , and $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively, although depending on pH of reaction solution [49]. Then, atomic 'Br or combined Br₂ might attack an aromatic ring to produce brominated compounds.

One more argument in this sense is the impact of the used incident ultrasonic frequency. Indeed, the rate of sono-bromination is higher at 480 kHz than at 36.6 kHz as shown in Fig. 1.

It is well known that the sonolysis of water is more effective at several hundreds kHz ultrasound than at several dozen kHz one [40,50] meaning that 'OH species might be involved in the whole mechanism. Moreover, *t*-butanol is known as a good hydroxyl radical scavenger [51]. Addition of 1.05 mmol of *t*-butanol quenched the reaction completely (entry 6, Table 2). A production of C₂Cl₄ and C₂Cl₆ was also decreased. This result clearly indicates that bromination takes place *via* radical mechanisms. Probably, 'OH is a key radical species, although oxidation of Br⁻ by 'Cl or HClO produced from the sonolysis of CCl₄ cannot be ruled out:

 $Br^- + \cdot Cl \rightarrow \cdot Br + Cl^-$

 $^{\textbf{\cdot}Br}+^{\textbf{\cdot}Br}\rightarrow Br_{2}$

 $Br^- + HClO \rightarrow Cl^- + OH^- + Br_2$

 $Br^- + HClO + HCl \rightarrow 2Cl^- + H_2O + Br_2$

As shown in entries 9 and 10 in Table 3, Br₂ is readily reactive to anisole under both sonication and mechanical stirring conditions. The resulted 2-/4-selectivities of entries 5, 9 and 10 were similar to each other. These results probably indicate that the main brominating species is Br₂. This point was clarified by a "blank" experiment. When aqueous CCl₄ with KBr in the absence of anisole was ultrasonically irradiated (480 kHz), the color of the CCl₄ layer became progressively dark brown. In 20-min sonication, 4.86×10^{-5} mol of Br₂ from 1.50×10^{-4} mol of Br⁻ was formed,



Fig. 1. The time profile of the production of bromoanisole and the consumption of anisole under experimental conditions; Anisole (0.1 mmol), KBr (0.15 mmol), CCl₄ (1 mL). H₂O (5 mL), time (1 h), ultrasonic powder (5 W). •, bromoanisole/480 kHz; \bigcirc , anisole recovered/480 kHz; \blacksquare , bromoanisole/36.6 kHz; \square , anisole recovered/36.6 kHz.

which was determined by UV at 417 nm (log ε = 2.32). When cyclohexene was then added to the brown solution, the color disappeared and bromocyclohexanol was obtained in 41% yield based on amount of generated Br₂, emphasizing the generation of Br₂ during the sonication.

What is the exact role of CCl_4 ? The production rate of I_2 from KI in the presence of CCl_4 is faster by 2 orders of magnitude than that in the absence of CCl_4 [43,52–54]. Zheng et al. proposed that added CCl_4 traps 'H so that 'H cannot recombine with 'OH [55] leading thus to an increase in 'OH concentration:

$$H + CCl_4 \rightarrow HCl + CCl_3$$

The increased concentration of OH by the presence of CCl_4 accelerates the oxidation of Br⁻, and thereby bromination occurs at meaningful rate. This may be the reason why CCl_4 is required.

The OH radicals can also recombine into H_2O_2 [37]. It has been reported that H_2O_2 or other oxidants can oxidize Cl⁻ to liberate molecular chlorine or HClO, which can chlorinate the active aromatic compounds [56,57]:

$$H_2O \xrightarrow{)))} OH + H$$

 ${}^{\boldsymbol{\cdot}}OH + {}^{\boldsymbol{\cdot}}OH \to H_2O$

 $H_2O_2 + HCl \rightarrow HClO + H_2O$

 $H_2O_2+2HCl \rightarrow Cl_2+2H_2O$

However, it is also reported that below 30% of H_2O_2 , chlorination does not proceed at all [57]. Since the production of such a high concentration of H_2O_2 by sonication cannot be expected [38], reaction mechanisms of our present system must be different from the above even if HCl (Cl⁻) was formed during sonolysis of aqueous CCl₄.

When KCl is used instead of KBr, chlorination occurred slightly faster than that without KCl (entries 1–4, Table 3). Selectivities of 2-/4- and monochloro-/dichloro-were not so affected. When KI is used, iodination occurred in 11% and 14% in respectively 1 and 2 h (entries 7 and 8, Table 3), but chlorination did not take place at all.

In the case of KI, color of CCl₄ layer of the reaction solution became persistently purple indicating that I_2 was formed during sonication [47,48]. However I_2 did not react well with anisole under our experimental conditions (entries 11 and 12, Table 3). Since only chlorination occurs without alkaline metal halide in H_2O –CCl₄ (entry 1, Table 3), all chlorinating species such as 'Cl or Cl₂ may be more preferably used to oxidize I^- to I_2 than to attack an aromatic ring.

Phenol, aniline, and acetanilide were also sono-brominated, as summarized in Table 4. Toluene and xylenes gave mainly α -brominated products. These results are similar to those by bromination with NaBr/H₂O₂/light [21]. Nitrobenzene was not brominated under the present sonication conditions. This result is generally observed at electrophilic bromination of electron-deficient arenes by Br₂.

The advanced oxidation process (AOP) [36-38] is characterized by production of the hydroxyl radical (\cdot OH) as a primary oxidant, which is used to depollute charged liquid effluents. However, the AOP must be used not only for degradation of persistent organic pollutants in aqueous effluents but also for the creation of more efficient chemical technologies. In the present study, ultrasonic AOP was applied for the bromination of aromatic compounds. Navarro, et al. showed that the sonolysis of HCOOH initiates Fisher–Tropsch hydrogenation of carbon monoxide [39]. In their case, the formation of CH₄ was explained by the secondary CO

| Table | 3 |
|-------|---|
|-------|---|

| Entry | Source of Halogen (mmol) | Time (h) | Anisole recovered (%) ^b | Monohaloanisole (%) (2-:4-) ^b | 2,4-Dihaloanisole (%) ^b |
|-----------------|------------------------------|----------|------------------------------------|--|------------------------------------|
| | | | | Chloroanisole | 2,4-Dichloroanisole |
| 1 | KCl 0.00 | 1.0 | 19 | 49 (30:70) | 22 |
| 2 | KCl 0.10 | 1.0 | 11 | 58 (28:72) | 23 |
| 3 | KCl 0.10 | 1.5 | 0 | 65 (30:70) | 34 |
| 4 | KCl 0.15 | 1.0 | 21 | 53 (28:72) | 20 |
| | | | | Bromoanisole | 2,4-Dibromoanisole |
| 5 | KBr 0.15 | 1.0 | 0 | 99 (3:97) | 0 |
| | | | | Iodoanisole | 2,4-Diiodoanisole |
| 6 | KI 0.15 | 0.5 | 89 | 2 (0:100) | 0 |
| 7 | KI 0.15 | 1.0 | 76 | 11 (8:92) | trace |
| 8 | KI 0.15 | 2.0 | 77 | 14 (8:92) | trace |
| | | | | Bromoanisole | 2,4-Dibromoanisole |
| 9 | Br ₂ ^c | 1.0 | 0 | 60 (4:96) ^d | 21 |
| 10 ^e | Br ₂ ^c | 1.0 | 13 | 84 (3:97) ^f | 0 |
| | | | | Iodoanisole | 2,4-Diiodooanisole |
| 11 | I ₂ ^c | 1.0 | 73 | 12 (8:92) ^f | 0 |
| 12 ^e | I ₂ ^c | 1.0 | 86 | 0 | 0 |
| | | | | | |

^a Anisole (0.1 mmol), CCl₄ (1 mL), H₂O (5 mL), ultrasound (480 kHz, 5 W).

^b GC analysis.

^c 0.075 mmol.

^d Chloroanisole was also formed at 19% (2-:4- = 0:100).

e Mechanical stirring.

^f Chloroanisole was not formed.

Table 4

Sonobromination of several aromatic compounds.^a

| Entry | Starting material | KBr (mmol) | Time (h) | Recovered starting material (%) ^b | Ring-brominated product (%) (2-:4-) ^b | Ring-dibrominated product (%) ^b | Benzylic brominated product (%) ^b |
|-------|----------------------|---------------|-------------|---|--|---|---|
| 1 | ⊘-он | 0.15 | 0.5 | 0 | 72 (25:75) | 0 | |
| 2 | | 0.15 | 0.5 | 15 | 12 (24:76) | 21 | |
| 3 | √ | 0.15 | 0.5 | 0 | 53 (79:21) | 17 | |
| 4 | | 0.15 | 1.0 | 0 | 34 (3:97) | 0 | |
| 5 | | 0.15 | 1.0 | 23 | 11 (41:59) | 0 | 64 |
| 6 | | 0.20 | 1.0 | 0 | 2 (49:51) | 0 | 93 |
| 7 | | 0.15 | 1.0 | 24 | 2 | 0 | 67 |
| 8 | \leq | 0.20 | 1.0 | 10 | 1 | 0 | 78 |
| 9 | | 0.15 | 1.0 | 16 | 28 | 0 | 41 |
| 10 | `\ | 0.20 | 1.0 | 0 | 8 | 0 | 47 |
| 11 | NO2 | 0.15 | 1.0 | 100 | 0 | | |

^a Starting material (0.1 mmol), CCl₄ (1 mL), H₂O (5 mL), ultrasound (480 kHz, 5 W).

^b GC analysis.

hydrogenation by hydrogen H₂ produced by sonolysis of water or HCOOH [58].

4. Conclusions

Aromatic compounds were brominated with KBr in CCl_4/H_2O by irradiation of ultrasound. The bromination does not occur under mechanical stirring conditions. It is assumed that the advanced oxidation process caused by ultrasound is the origin of the bromination of the aromatic compounds. Namely, H_2O and/or CCl_4 are sonolyzed to generate radical species such as 'OH and 'Cl. The radical species oxidize Br^- to produce brominating agents, which attack an aromatic ring. So far, the reactivity of brominating agents produced ultrasonically is similar to that of Br_2 .

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