

# Environmental Applications of Ultrasound

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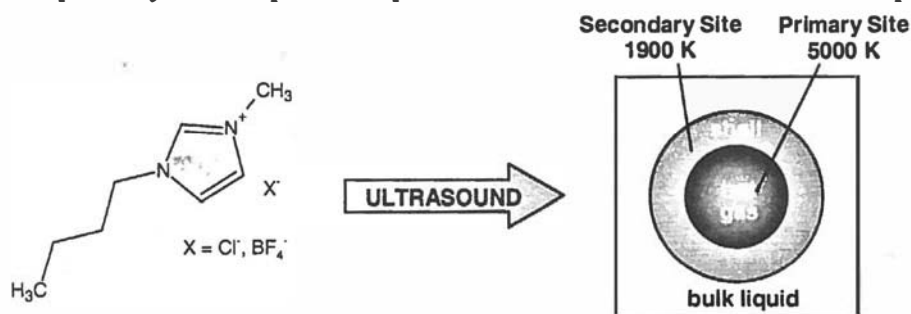
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Environmental and ultrasonic sciences are independently well established and studied. The combination of the two areas results in a field that is less understood and deserves attention as our global environment continues to deteriorate. The application of ultrasound to environmental problems relies on the process of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. The collapse of such bubbles creates hot spots with temperatures as high as 5000 K, pressures up to 800 atm, and cooling rates in excess of  $10^{10}$  K/s.<sup>1,2</sup> These conditions are responsible for a variety of ultrasonic chemical and physical effects.<sup>3,4</sup> Investigated environmental applications include the use of ultrasound for the dissolution of gas into water, the sonochemistry of ionic liquids, and the preparation of nanostructured materials for the catalytic hydrodehalogenation of organic halides.

## Sonochemistry and Sonoluminescence of Ionic Liquids

Room-temperature ionic liquids were examined for their potential application as solvents for sonochemical reactions.<sup>5-7</sup> Widely studied *N,N'*-dialkylimidazolium ionic liquids possess unique properties, such as high thermal stability, negligible vapor pressure, and wide liquid temperature range, which are ideal for sonochemical reactions. The effects of ultrasound on room-temperature ionic liquids were investigated using butylmethyl imidazolium chloride (BuMeImCl), butylmethyl imidazolium tetrafluoroborate, and decylmethyl imidazolium tetraphenylborate. Gas-chromatography mass-spectrometry head-gas analysis and multibubble sonoluminescence (MBSL) were used to establish that room-temperature ionic liquids decomposed in the presence of ultrasound. The head-gas over sonicating ionic liquids contained products associated with the decomposition of the imidazole and anionic component. The MBSL spectrum of BuMeImCl contained molecular emission from excited states of  $C_2^*$  and  $CH^*$ . The decomposition mechanism was determined to be a combination of factors related to the two-site model of sonochemical reactions, shown in Figure 1. Initial decomposition of the ionic liquid occurred around the outer shell of a collapsing bubble (~1900 K) resulting in the formation of imidazoles and, in the case of BuMeImCl, alkylhalides. The volatility of these primary decomposition products allowed for further decomposition



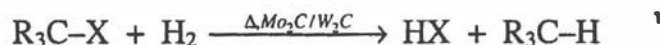
within the primary gas/vapor phase of the bubble (~5000 K).

**Figure 1.** Two-site model for sonochemical reactions and the decomposition of ionic liquids.

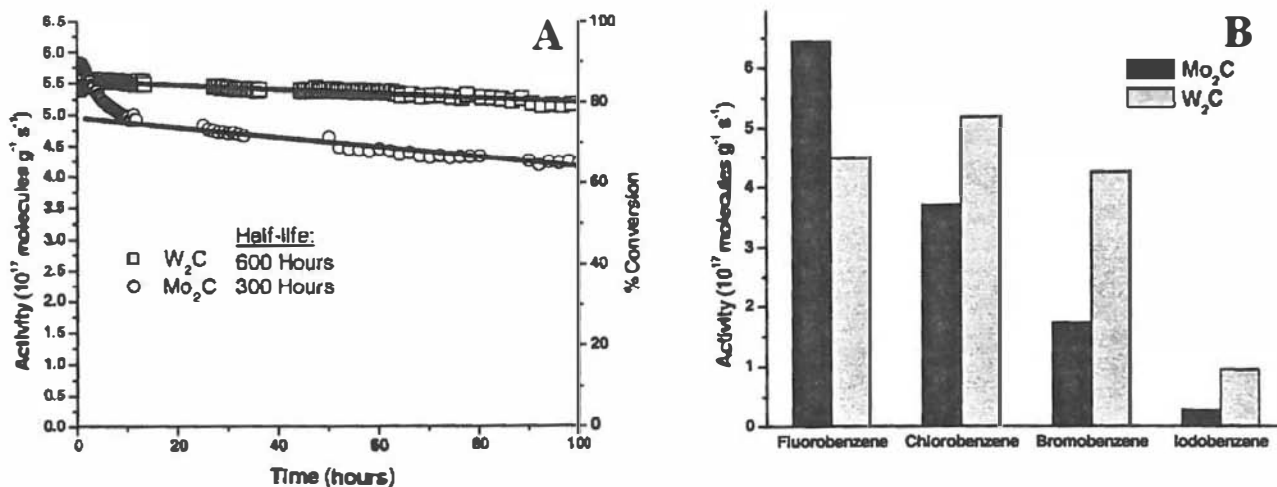
The sonochemical solvent properties of room-temperature ionic liquids were compared to hexadecane for the preparation of nanostructured materials. The sonication of methylcyclopentadienyl manganese tricarbonyl in hexadecane formed an amorphous oxycarbide powder. A similar sonication carried out in BuMeImCl resulted in the formation of crystalline manganese oxide (MnO) with N, C, and Cl impurities. Likewise, sonication of the same organometallic compound in BuMeImBF<sub>4</sub> resulted in the production of a mixture of crystalline MnO and manganese fluoride (MnF<sub>2</sub>) with N, C, and B impurities. The crystallinity and impurities demonstrate two primary disadvantages of using room-temperature ionic liquids as sonochemical solvents.

### Hydrodehalogenation with Sonochemically Prepared Mo<sub>2</sub>C and W<sub>2</sub>C

As previously reported, molybdenum hexacarbonyl and tungsten hexacarbonyl were decomposed sonochemically in hexadecane to form porous aggregates of 2-3 nm high surface area Mo<sub>2</sub>C and W<sub>2</sub>C nanoparticles.<sup>8</sup> The activity of these materials was studied for the catalytic hydrodehalogenation (HDH) of aliphatic and aromatic halocarbons at low temperatures (T = 200-300°C).<sup>9</sup> Volatile substrates were studied using a gas/vapor phase fixed-bed catalytic microreactor system and non-volatile substrates were studied using a pressurized batch reactor. Both catalysts were selective, active, and stable for most substrates tested.

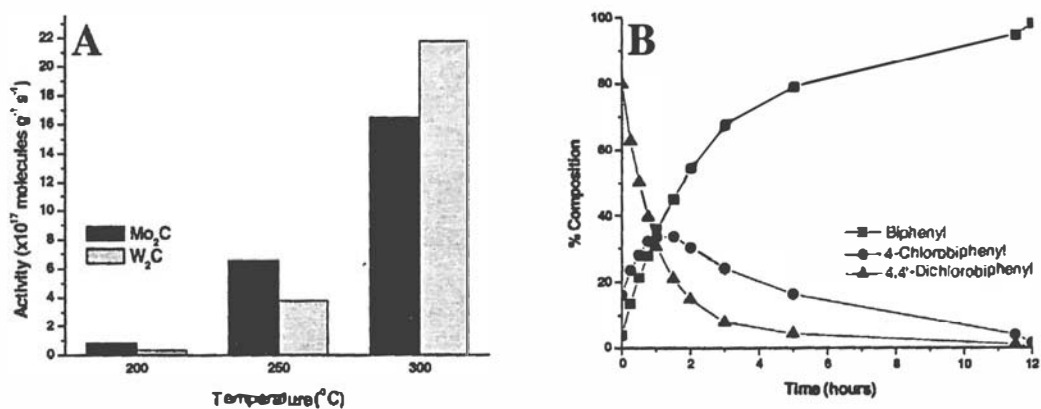


Chlorobenzene was used as an initial model of polychlorinated biphenyls (PCBs) and used to probe the catalysts HDH stability and selectivity. Both Mo<sub>2</sub>C and W<sub>2</sub>C were shown to be active for temperatures 200-300°C, selective for benzene only, and stable with half lives of up to 600 h (Figure 1A). Benzene was also the only observed product for the HDH of fluoro-, chloro-, bromo- and iodobenzene, with activities following the general trend of C<sub>6</sub>H<sub>5</sub>F > C<sub>6</sub>H<sub>5</sub>Cl > C<sub>6</sub>H<sub>5</sub>Br > C<sub>6</sub>H<sub>5</sub>I as shown in Figure 1B. Studies carried out with 1-chlorobutane and 1-chloropropane under similar conditions exhibited HDH rates approximately an order of magnitude greater than chlorobenzene.



**Figure 2.** (A) Stability of Mo<sub>2</sub>C and W<sub>2</sub>C for the HDH of chlorobenzene. (B) Catalytic activity of Mo<sub>2</sub>C and W<sub>2</sub>C for the HDH of halobenzenes.

The sonochemically prepared catalysts were also shown to be active for the HDH of major environmental contaminants such as dichlorodifluoromethane, tetrachloroethylene, 4,4'-dichlorobiphenyl, polychlorinated diphenylether, 4,4'-dibromobiphenyl, trichlorophenol, and 1,1,1-trichloro-2,2-bis(*p*-chlorobiphenyl)ethane (DDT). For the HDH of chlorofluorocarbons (CFCs), Cl was selectively removed over F and alkanes (up to 50%) were the major products. In the liquid phase, the HDH of polychlorinated and polybrominated biphenyls resulted in biphenyl as the only product with activity greater than the gas/vapor phase studies (Figure 3). Similarly, the HDH of halogenated diphenyl ethers were selective for diphenyl ether. Characterization of post catalytic materials with x-ray powder diffraction and x-ray photoelectron spectroscopy revealed no change in the bulk structure of the catalyst and chlorination of the surface



metal species, respectively.

**Figure 3.** (A) Catalytic activity of Mo<sub>2</sub>C and W<sub>2</sub>C for the HDH of 4,4'-dichlorobiphenyl. (B) Composition of products from the HDH of 4,4'-dichlorobiphenyl with W<sub>2</sub>C.

## References

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