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SONOCHEMISTRY - A REVIEW.

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1. INTRODUCTION

It is not very often that the opportunity arises for a chemist to move into a brand new field of research. An increasing number of scientists however are now becoming interested in just such a new field - sonochemistry - used to describe the effect of ultrasonic sound waves on chemical reactivity. The drawbacks to most new scientific developments are that they require expensive or specialised apparatus and a considerable degree of expertise in a particular field of study. What makes research in sonochemistry so appealing is that it is quite inexpensive to get started and power ultrasound has found applications over the whole range of chemistry.

For many years ultrasound has found a wide variety of uses in engineering, science and medicine but its applications to chemistry have only recently come to the fore [1]. Several reviews on the chemical applications of ultrasound have been published recently [2,3,4].

2. THE CHEMICAL EFFECTS OF POWER ULTRASOUND

Chemical transformations can be produced by ultrasonic irradiation provided that the intensity is high enough to produce cavitation within the medium through which it passes, consequently the medium must have a liquid component. Generally the frequency range employed to induce such reactions lies between 20 to 100kHz *i.e.* the range normally employed for cleaning and plastic welding.

The violent collapse of ultrasonically induced cavitation bubbles occurs with the release of large amounts of energy in the immediate vicinity of these microbubbles. It has been estimated that temperatures of up to several thousand Kelvin and pressures of several hundred atmospheres are produced during this collapse. The mechanical and chemical effects of the collapsing bubble will be felt in three distinct regions (a) within the bubble itself which can be thought of as a high pressure and temperature microreactor (b) in the liquid region immediately adjacent to the bubble where the temperatures are not so great and (c) in the immediate vicinity of the bubble where the shockwave produced on collapse will create enormous shear forces. These effects can be summarised in terms of three different reaction types.

2.1 Homogeneous Reactions.

The microbubble (or cavitation bubble) formed in the rarefaction cycle does not enclose a vacuum - it contains vapour from the solvent or any volatile reagent present so that, on collapse, these vapours are subjected to the enormous increases in both temperature and pressure referred to above. Under such extremes the solvent and/or reagent suffers fragmentation to generate reactive species of the radical or carbene type. Thus if water is sonicated then the extreme conditions generated on collapse of the cavitation bubbles are sufficient to cause rupture of the O-H bond itself with the formation of radical species and the subsequent production of oxygen gas and hydrogen peroxide (Scheme 1) [5].

$$
\begin{array}{lll}
H_2O & \text{----------}\rangle & H\cdot + \cdot OH \\
H\cdot + O_2 & \text{----------}\rangle & HO_2\cdot \\
HO_2\cdot + HO_2\cdot & \text{----------}\rangle & H_2O_2 + O_2 \\
HO\cdot + \cdot OH & \text{----------}\rangle & H_2O_2 \quad \text{...... Scheme 1}
\end{array}
$$

Any species dissolved in the water is clearly going to be subject to chemical reaction with these ultrasonically produced radicals and/or hydrogen peroxide, thus if iodide ion is present in solution elemental iodine will be liberated.

The shock wave produced on bubble collapse, can disrupt solvent structure and this can influence reactivity by altering solvation of the reactive species present. An example of this is to be found in the ultrasonically assisted reaction of 2-chloro-2-methylpropane in aqueous alcoholic media (Scheme 2) where sonochemical rate enhancements of up to 20 fold have been reported [6]. The sonochemical effect increases with an increase in ethanol content of the solvent and this is consistent with the destruction of solvent structure (which also increases with ethanol content).

$$(CH_3)_3C\text{-}Cl \;\langle{=}{=}{=}{=}\rangle\; (CH_3)_3C^+ + Cl^- \text{ ----}\rangle\; CH_3)_3C\text{-}OH + HCl \text{ ... Scheme 2}$$

As with many sonochemical studies the effect of irradiation in this solvolysis decreases as the reaction temperature is increased. This general observation is related to a decrease in the energy of cavitational collapse as the solvent vapour pressure is raised. In simple terms the more vapour which enters the cavitation bubble the more of a cushion it will provide against violent collapse.

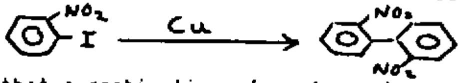
2.2 Heterogeneous Reactions Involving a Solid/Liquid Interface.

There are two types of reaction involving solid/liquid interfaces (i) in which the solid is a reagent and is consumed in the process and (ii) in which the solid - often a metal - functions as a catalyst.

2.2.1 Solid as Reagent. A classic use of ultrasound is in the initiation and enhancement of organometallic reactions. One such example is the preparation of a Grignard Reagent - an organomagnesium halide (Scheme 3). A long-standing problem associated with Grignard reagent synthesis is that in order to facilitate reaction between the organic halide and the metal in an ether solvent all of the reagents must be dry and the surface of the magnesium must be clean and oxide free. Such conditions are difficult to achieve and so many methods of initiating the reaction have been developed most of which rely on adding activating chemicals to the reaction mixture. The modern method of initiating the reaction is by sonication which avoids the need for the addition of chemical activators. Even in damp, technical grade ether ultrasonic irradiation can initiate the reaction in under 4 minutes whereas with conventional methodology initiation required several hours [7]. This is potentially of great economic importance to industry indicating that in some situations sonication may remove the need to employ super-pure chemicals.

$CH_3-CH_2-CH(Br)-CH_3 + Mg \dashrightarrow CH_3-CH_2-CH(MgBr)-CH_3$ ...... Scheme 3

When examined by electron microscopy surfaces of metals which have been subjected to ultrasonic irradiation reveal "pitting" looking not unlike craters on the moon [8]. This pitting serves both to expose new surface to the reagents and to increase the effective area available for reaction. The pitting is the result of two processes: (i) the implosion of cavitation bubbles formed from gases or impurities on the surface of the metal and (ii) the generation of a jet of solvent which impinges on the surface when a cavitation bubble collapses close to it. If the metal reagent is in the form of a powder then sonication can cause particle rupture with a consequent decrease in particle size and increase in surface area available for reaction.



...... Scheme 4

Evidence that a combination of surface cleaning and an increase in surface area cannot fully explain the extent of the sonochemically enhanced reactivity is provided by the Ullmann coupling reaction. The reaction of 2-iodonitrobenzene to give a dinitrobiphenyl using conventional methodology requires heating for 48h and the use of a 10 fold excess of copper powder (Scheme 4). The use of power ultrasound affords a similar (80%) yield in a much shorter time (1.5h) using only a four fold excess of copper [9]. During these studies it was observed that the average particle size of the copper fell from 87um to 25um but this increase in surface area was shown to be insufficient to explain the large (50 fold) enhancement in reactivity produced by ultrasonic irradiation.

2.2.2 Catalytic Reactions. One of the more familiar catalytic reactions is the addition of hydrogen to an unsaturated compound - hydrogenation. It has been found possible, for example, to promote hydrogenation *via* the decomposition of hydrazine using palladium-on-charcoal and low power ultrasound [10]. Results obtained under sonication at room temperature for the total hydrogenation of diphenylacetylene (2h) (Scheme 5) appear to be almost as good as those obtained under traditional reflux conditions and are substantially better than obtained simply by stirring at 25°C (6h).

Ph-C=C-Ph ----(N_2H_2/Pd)----> Ph-CH_2-CH_2-Ph ...... Scheme 5

2.3 Heterogeneous Reactions Involving Liquid/Liquid Interfaces. In aqueous/organic mixtures it is only in the interfacial region where a reaction between reagents dissolved in different phases can occur. In such situations the synthetic chemist will normally use a phase transfer catalyst (PTC) to transfer a reagent from one phase to another. There are however two drawbacks to the use of phase transfer catalysts (i) the PTC itself is generally expensive and (ii) a PTC is potentially dangerous in that it can, by its very nature, catalyse the transfer of chemicals into human tissue. This has led to the use of ultrasound to enhance the activity of or even replace completely the use of a PTC because sonication generates extremely fine emulsions which result in very large interfacial contact areas between the liquids and a corresponding dramatic increase in the reactivity between species dissolved in the separate liquids. An additional feature of sonication is that the sonicated emulsion is continuously subject to mechanical vibration - enhancing any transfer between phases. A good example of this type of application is to be found in the hydrolysis of commercially important oils, fats and waxes (Scheme 6) [11]. Under sonochemical conditions the hydrolyses can be carried out at lower temperatures leading to cleaner products.

...... Scheme 6

3. CONCLUSION

A synthetic chemist might therefore expect to use ultrasound for a range of applications and perhaps achieve one or more of a number of the beneficial effects below:

1. to accelerate a reaction or permit use of less forcing conditions
2. to enhance catalyst efficiency
3. to make use of cruder reagents
4. to initiate reaction or reduce any induction period involved.

4. REFERENCES

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