Sonochemistry : Past, present and future

Suresh C. Ameta*, Pinki B. Punjabi, Harish Swarnkar, Neeru Chhabra and Madhu Jain

Department of Chemistry, College of Science, Sukhadia University, Udaipur-313 001, India

Manuscript received 2 April 2001

The term ultrasound is very common in reference of animal communications (bats, dog whistles), medical diagnosis (foetal scanning, treatment of muscle strains), cleaning and drilling of teeth, plastics and metals welding and underwater ranging (SONAR), etc. Ultrasound is defined as sound of a frequency, which is beyond human hearing, i.e. above 16 kHz. It has been recently reported that chemical reactivity of a system increases on irradiating it with power ultrasound. The study of effects of ultrasound on chemical reactivity is termed as sonochemistry.

Many sonicators are useful for the production of ultrasound. The important ones are : ultrasonic cleaning bath, ultrasonic probe system, the cuphorn system, the flow cell system, the submersible transducer assembly, the whistle reactor, the tube reactor and ultrasonic interferometer, etc. There are two distinct ranges of ultrasound : diagnostic (for physical measurements) and power (to influence chemical reactivity). After the Titanic disaster of 1912, it was suggested that the distance of an iceberg from a ship could be easily estimated from the time lapse between emitting a sound from a ship and receiving an echo from the iceberg. Thus the pulse/echo ranging technique or diagnostic ultrasound developed for the location of submarines and later, this technique led to SONAR (*SOund, Navigation And Ranging*) and flaw detection in metals and other materials. Diagnostic ultrasound can be used for chemical analysis particularly for remote sensing in flow system.

Sir John Thornycroft and Sidney Barby characterized an effect called cavitation through which power ultrasound influences the chemical reactivity of a system. It is known that sound is transmitted through a fluid as a wave consisting of alternating compression and rarefaction cycles. This creates an acoustic pressure in the medium, which varies with time. This acoustic intensity is the energy transmitted through 1 m² of fluid per unit time, which will vary with distance from its source due to attenuation caused by viscous forces and resulting in heating of the liquid.

Sonation causes enhanced molecular motion and this leads to very efficient mass transfer and mixing and so can enhance many chemical reactions. If the negative pressures

during the rarefaction phase of the waves are sufficiently large, then the liquid will be 'torn apart', which results in the formation of voids or bubbles – this process is known as cavitation. This may occur at pressures much less than those required overcoming the tensile strength of a liquid since there are always minute dust particles or dissolved gases present, which act as nucleating sites. During its growth, dissolved gases and/or solvent vapour may diffuse into the bubble. Sonication is very effective for degassification as any dissolved gases or gas bubbles will not easily collapse in the compression cycle and it will continue to grow on further rarefaction cycles, filling with more gas and finally floating to the surface. Since the rarefaction cycles are taking place very rapidly, and hence, the bubbles grow so quickly that degassing appears to occur almost instantaneously.

In a cavitating system, three different zones can be identified : (i) the bulk liquid, in which no primary sonochemical activity takes place, (ii) the center of the bubble, where the harsh conditions cause reactions in vapours and gases, and (iii) the interfacial region, where there are large variations in temperature and pressure gradients and also very high shear gradients due to shock waves and motion of solvent molecules around the collapsing bubbles.

Many factors affect cavitation. Most of the sonochemical work has been done having frequencies around 20–50 kHz. The sonochemical effects is very less at higher frequencies because then the bubbles has limited time to grow and collapse. The sonochemical activity rises with increasing ultrasound intensity but this efficiency falls in many reactions above a particular optimum intensity. Highly soluble gases reduce the cavitation threshold of a liquid but these also lead to greater amounts of gases entering the bubbles; thus, resulting in a 'cushioning' of the collapse and as a consequence, reducing sonochemical activity. Higher sonochemical activity is obtained in solvents with low vapour pressures. Solvent with high densities, surface tensions and viscosities generally have a higher threshold for cavitation but more harsh conditions appear once cavitation begins. A very large sonication effect has been observed at lower temperatures.

Ultrasonic homogenization and emulsification can be applied in the synthesis of polymers by emulsion and suspension polymerization. It can also be used in the food industry for the processing of tomato ketchup, etc.

Synthetic sonochemical reactions

Ultrasound gives a way of energizing a chemical system along with the more classical methods such as, thermal, photochemical and electrochemical. Ultrasound opens up new synthetic routes for synthetic organic chemistry, improves regio- and stereoselectivity of reactions, increases the ability to manipulate selected functional groups without affecting other groups. The application of ultrasound will increase the rate of heterogeneous reactions by aiding mass transfer and reactions involving metals by cleaning and activating their surfaces. Many sonochemical reactions have been proposed. Some of these are described below.

Reduction :

The use of ultrasound favoured the reduction of aromatic hydrocarbons to their radical anions by alkali metals. The ultrasound cleans the surface of the metal by removing the layer of metal hydroxide present on it and breaks up the pieces of metals. A recent example of one electron reduction¹ is

Torok *et al.*² reported sonochemical enantioselective hydrogenation of ethyl pyruvate over platinum catalyst.

Alkylation :

Ultrasound enhances the rate of these reactions and improves the yields and purity of products. A very useful alkylation reactions is the preparation of diazacorand³.

Ester hydrolysis :

Methyl 2,4-dimethylbenzoate on alkaline hydrolysis gives 2,4-dimethylbenzoic acid⁴. The following results show the beneficial use of ultrasound in this reaction :

Time of reaction, min.	90	10	60
Condition	Reflux	Ultrasound	Ultrasound
Yield% of 2,4-dimethylbenzoic acid	15	15	94

The use of ultrasound is also advantageous in the hydrolysis of naturally occurring oils and waxes and in this manner the amount of side-products is reduced. Time can be reduced for the completion of reaction by using ultrasound. Ultrasound reduces the particle size of the oil droplets, which is an essential part of emulsification.

Generation of reactive intermediates :

In this dehalogenation reaction, carbene is formed in the presence of zinc⁵. But if this reaction is carried out with ultrasound, it cleans the surface of the zinc, transports reagents to its surface and products away from the surface and generates smaller zinc particles.

Diels-Alder reaction :

This reaction does not involve single electron transfer process. Lee and Snyder^{6,7} reported the appreciable effect of ultrasound on the rate of the Diels-Alder reaction.

This reaction synthesizes abietanoid pigments, which are responsible for the biological activity of the Chinese traditional medicine Dan Shen. Under sonication of the reaction mixture, the yields of the products increase.

Low⁸ examined the reaction of anthracene with maleic anhydride in toluene. The reaction was completed within 4 h when a direct immersion microtip probe was used. The

equivalent thermal reaction is very slow than the sonochemical reaction and was only 11% complete after the same period of time.

Sonochemical generation of organoiron complexes :

π -Allyltricarbonyliron lactone complexes are intermediates, which will further synthesize cyclic lactones^{9,10} and lactams¹¹. The yields of ferrilactone complex obtained from the thermal reaction with $\text{Fe}(\text{CO})_4$.THF and the sonochemical reaction with $\text{Fe}_2(\text{CO})_9$ in benzene are compared¹².

Barbier reaction :

Improved Barbier reaction involves the reaction of a ketone with alkyl halide in presence of lithium to give the corresponding alcohol with introduction of the alkyl group on carbon of carbonyl group¹³.

Unusual Barbier reaction was also reported, where it proceeds in presence of zinc¹⁴.

Barbier reaction was modified and some interesting results were obtained depending on the nature of halogen in alkyl halide. Ketone is the major product on using alkyl chloride, while no ketone was obtained in presence of alkyl iodide, rather benzil was formed with a yield of 40%¹⁵.

Photochemistry with ultrasound :

Photochemistry can be carried out in the presence of TiO_2 where a chemical reaction can be initiated by substrate absorption onto a UV-activated surface, e.g. oxidation of sul-

fides to sulfones and sulfoxides¹⁶. The dechlorination¹⁷ of pentachlorophenol in the presence of 0.2% TiO_2 is very efficient in UV-radiation. When ultrasound is used in conjunction with this, the rate of photolytic dechlorination is enhanced. This is because sonochemistry promotes the surface cleaning, particle size reduction and increase mass transfer to the powder surface.

Miscellaneous reaction :

Ketones on reductive deoxygenation gives alkenes by low valent titanium compounds. But in this case, the reaction will take place at much milder conditions, if ultrasound is used¹⁸.

Ultrasound can be used to initiate the formation of Grignard reagents. Magnesium can reduce anthracene under the influence of ultrasound¹⁹.

The above reaction of the formation of allylstannanes from allyl halide and stannyl halide will give very low yield. However, if the same reaction is done in the presence of magnesium and ultrasound, the high yield and purity of the product will be obtained, which is synthetically very important²⁰.

The generation of perfluoroalkyl zinc halides²¹, and facilitating the Reformatsky reaction²² are the example, in which the reaction will not take place in the absence of ultrasound²³. Luche *et al.*²⁴ initiated to apply the zinc-copper coupled derived reagents, in synthetic organic chemistry using ultrasound. A strong evidence has been proposed in favour of single electron transfer in these reactions. Ultrasound enables zinc and acetic acid to reduce carbon-carbon double bonds of unsaturated esters and quinones²⁵. The reduction of diarylketones by zinc in presence of aluminium trichloride leads to reductive coupling²⁶.

Ultrasound can be utilized to activate platinum²⁷, palladium²⁸ and nickel²⁹. The activation of nickel of ultrasound

is recently reported in the hydrogenolysis of N-N bond of hydrazines³⁰ and in catalyzing the hydrosilylation of alkenes³¹. Raney nickel modified by interaction with tartaric acid and sodium bromide is transformed into an enantioselective catalyst by the application of ultrasound³², which can reduce β -ketoesters and β -diketones with high enantioselectivity. These results provide a method that will quite effectively compete with enzymatic methods.

There are some reactions, which in the presence of ultrasound do not involve single electron transfer processes. For example, conversion of aryl diazonium salts to aryl ethers³³, reaction of sulfonyl azides with alkenes³⁴, generation of ketones³⁵ and the reduction of esters by zinc borohydride³⁶.

Bhatkhande and Samant³⁷ observed ultrasonic assisted PTC catalyzed saponification of vegetable oils using aqueous alkali. Sonochemical degradation of ethylbenzene in aqueous solution was studied by Visscher *et al.*³⁸. Drijver *et al.*³⁹ studied organic intermediates in sonolysis of chlorobenzene in aqueous solution. Petrier *et al.*⁴⁰ reported ultrasound and environment sonochemical destruction of chloroaromatic derivatives. Gaplovsky *et al.*⁴¹ reported the effects of ultrasound on the photopinacolization of benzophenone. Ultrasound assisted heterogeneous permanganate oxidations were studied by Meriarova *et al.*⁴². Under sonic conditions, the reductive dehalogenation of α -haloketones with zinc in presence of ammonium salts was studied by Rama *et al.*⁴³. Lorimer *et al.*⁴⁴ reported the dye effluent decolourization using ultrasonically assisted electro-oxidation. Nagata *et al.*⁴⁵ reported sonochemical degradation of chlorophenols in water. Rong *et al.*⁴⁶ studied simple quantification of ultrasonic intensity using aqueous solution of phenolphthalein. Mizukoshi *et al.*⁴⁷ studied the role of surfactants in the preparation of platinum nanoparticles by sonochemical reduction of the Pt^{IV} ions.

Polymers

There are various fields, where ultrasound is beneficial in the preparation of polymeric materials. Under sonochemical conditions several synthetic methods are accelerated but the greatest effects are in the molecular weight distributions of the resulting polymers. Pethrick⁴⁸ reviewed that high fre-

quency ultrasound in the range of 1–10 MHz is applied to the determination of structure and conformation of polymers, while low frequency ultrasound provides information on both polymerization and depolymerization.

The modification of exciting polymers into new materials is a degradation process. Its mechanism is described as the polymer chain being caught in the rapid flow of solvent molecules about collapsing and exploded cavitation bubbles and being subjected to extremely large shear forces. The rate and extent of degradation may be maximized by saturating the polymer solution with gas, employing a gas with a low solubility, using a solvent with a low vapour pressure, reducing the experimental temperature and insonation frequency, increasing the intensity of irradiation and decreasing the solution concentration. Thermal degradation produces cleavage in a random process while in ultrasonic degradation cleavage occurs preferentially near the middle of the chain. Melville and Murray⁴⁹ showed the presence of radical intermediates in the degradation.

Emulsion or suspension polymerization is another process for preparing polymers⁵⁰. Lorimer *et al.*⁵¹ compared styrene polymerization carried out in the presence and absence of ultrasound from a high intensity horn. They observed that the decomposition of potassium persulfate was accelerated and which in turn, increased the rate of polymerization together with the production of more stable emulsions.

Leboun and Porte⁵² illustrated the ring opening reactions of octamethyltetrasiloxane to poly(dimethylsiloxane) (PDMS) catalyzed by sulfuric acid.

This is the base material of the large number of silicon products.

sufficient time for α -elimination.

Change in the metal will lead to a change in yields of products. In this case, if lithium, sodium and potassium are used, the percentage yield of product (C) decreases and product (D) increases, respectively.

If we go down in the group of halogens, the percentage yield of product (E) decreases and that of product (F) increases.

It was proved experimentally that in some cases a 'silylenoid' was formed as an intermediate.

Transition metal catalyzed reactions of silanes :

It was demonstrated that platinum on carbon catalyze hydrosilation.

However, if ultrasound is used, high yield of product was obtained and by distilling off the products, catalyst may also be reused²⁷.

Boudjouk and Hauck⁵⁸ examined alkynes by this reaction.

If nickel powder, freshly prepared from nickel halide and lithium in the presence of ultrasonic waves, is used, it catalyzes hydrosilylation very efficiently. In the absence of an olefin, this activated form of nickel will catalyze the dehydrogenation coupling of silicon hydrides to form Si-Si bond³¹.

Future prospects

Ultrasound has certain advantages in electrochemistry

as it keeps electrodes clean and degasses electrode surface⁵⁹. Sonochemical process will replace current methodology in polymer synthesis. Ultrasound can produce many polymers without the need of initiators or emulsifiers, etc. Del Campo *et al.*⁶⁰ studied low temperature sonoelectrochemical processes : mass transport and cavitation effects of 20 kHz ultrasound in liquid ammonia. Masti *et al.*⁶¹ observed room temperature sonoelectrochemical synthesis of molybdenum sulfide. Low power ultrasonic irradiation of media assists in the rate of growth and yield of algal cells⁶². A combination of photochemistry with sonochemistry has also been used for the treatment of waste waters¹⁷. Patent issued in the sonochemical synthesis of 1-aminoanthraquinone reflects the growing interest in the field⁶³. Sonochemistry is a developing field with a number of such frontiers and a much wider range of applications will come out in the years to come. Recently, the buckyball fullerene has also been synthesized, utilizing a sonochemical route⁶⁴. Petrier and Francony⁶⁵ studied incidence of wave frequency on the reaction rates during ultrasonic wastewater treatment.

References

1. P. Boudjouk and B. H. Han, *J. Catal.*, 1983, **79**, 489.
2. B. Torok, K. Felfoldi, G. Szakonyi, K. Balazsik and M. Bartok, *Catal. Lett.*, 1997, **4**, 301.
3. J. Jurczak and R. Ostaszewski, *Tetrahedron Lett.*, 1998, **29**, 959.
4. S. Moon, L. Duchin and J. V. Cooney, *Tetrahedron Lett.*, 1979, 3917.
5. O. Repic and S. Vogt, *Tetrahedron Lett.*, 1982, **23**, 2729.
6. J. Lee and J. K. Snyder, *J. Am. Chem. Soc.*, 1989, **111**, 1522.
7. J. Lee, H. S. Mei and J. K. Snyder, *J. Org. Chem.*, 1990, **55**, 5013.
8. C. M. R. Low in "Current Trends in Sonochemistry", ed. G. J. Price, Royal Soc. Chem., Cambridge, 1992, pp. 66-67.
9. S. V. Ley, *Phil. Trans. R. Soc. London, Ser. A*, 1988, **326**, 663.
10. R. Aumann, H. Ring, C. Kruger and R. Goddard, *Chem. Ber.*, 1979, **112**.
11. S. T. Hodgson, D. M. Hollinshead, S. V. Ley, C. M. R. Low and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2375.
12. R. W. Bates, D. Diez-Martin, W. J. Kerr, J. G. Knight, S. V. Ley and A. Sakellariadis, *Tetrahedron*, 1990, **46**, 4063.
13. N. F. Scilly, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1655.
14. C. Dupuy, C. Petrier, C. Allavena and J. L. Luche, *Tetrahedron Lett.*, 1986, **27**, 3149.
15. J. C. de Souza Barboza, J. L. Luche and C. Petrier, *Tetrahedron Lett.*, 1987, **28**, 2013.
16. R. S. Davidson and J. E. Pratt, *Tetrahedron Lett.*, 1983, **24**, 5903.
17. T. J. Mason in "Current Trends in Sonochemistry", ed. G. J. Price, Royal Soc. Chem., Cambridge, 1992.

18. S. K. Nayak and A. Banerji, *J. Org. Chem.*, 1991, **56**, 1940.
19. W. Oppolzer and P. Schneider, *Tetrahedron Lett.*, 1984, **25**, 3305.
20. Y. Naruta, Y. Nishagaichi and K. Maruyama, *Chem. Lett.*, 1968, 1957.
21. T. Kitazume and N. Ishikawa, *J. Am. Chem. Soc.*, 1985, **107**, 5186.
22. R. W. Land and B. Schaub, *Tetrahedron Lett.*, 1988, **29**, 2943.
23. T. Kitazume, *Synthesis*, 1986, 855.
24. J. L. Luche, A. Allavena, C. Petrier and C. Dupuy, *Tetrahedron Lett.*, 1988, **29**, 5373.
25. A. P. Marchand and G. M. Reddy, *Synthesis*, 1991, 198.
26. R. Sato, T. Nagaoka and M. Saito, *Tetrahedron Lett.*, 1990, **31**, 4165.
27. B. H. Han and P. Boudjouk, *Organometallics*, 1983, **2**, 769.
28. K. Imi, K. Imai and K. Utimoto, *Tetrahedron Lett.*, 1987, **28**, 3127.
29. K. J. Moulton, S. Koritala and E. N. Frankel, *J. Am. Oil Chem. Soc.*, 1983, **60**, 1257.
30. A. Alexakis, N. Lensen and P. Mangeney, *Syn. Lett.*, 1991, **9**, 625.
31. P. Boudjouk, B. H. Han, J. R. Jacobsen and B. J. Hauck, *J. Chem. Soc., Chem. Commun.*, 1991, 1424.
32. A. Tai, T. Kikukawa, T. Sugimura, Y. Inoue, T. Osawa and S. Fujii, *J. Chem. Soc., Chem. Commun.*, 1991, 795.
33. G. Olah and A. H. Wu, *Synthesis*, 1991, 204.
34. D. Goldsmith and J. J. Sorm, *Tetrahedron Lett.*, 1991, **32**, 2457.
35. J. Pan, I. Hanna and J. Y. Lallenand, *Tetrahedron Lett.*, 1991, **32**, 7543.
36. C. Ranu and M. K. Basu, *Tetrahedron Lett.*, 1991, **32**, 3243.
37. B. S. Bhatkhande and S. D. Samant, *Ultrason. Sonochem.*, 1998, **5**, 7.
38. A. De Visscher, H. Van Langenhove and P. Van Eeoo, *Ultrason. Sonochem.*, 1997, **4**, 145.
39. D. Drijvers, H. V. Langenhove and K. Vervaet, *Ultrason. Sonochem.*, 1998, **5**, 13.
40. C. Petrier, Y. Jiang and M.-F. Lamy, *Environ. Sci. Technol.*, 1998, **32**, 1316.
41. A. Gaplovsky, M. Gaplovsky, S. Toma and J.-L. Luche, *J. Org. Chem.*, 2000, **65**, 8444.
42. M. Meciarova, S. Toma and A. Heribanova, *Tetrahedron*, 2000, **56**, 8561.
43. K. Rama, E. Nagendra and M. A. Pasha, *Indian J. Chem., Sect. B*, 2000, **39**, 563.
44. J. P. Lorimer, T. J. Mason, M. Plattes and S. S. Phull, *Ultrason. Sonochem.*, 2000, **7**, 237.
45. Y. Nagata, M. Nakagawa, H. Okuno, Y. Mizukoshi, B. Yim and Y. Maeda, *Ultrason. Sonochem.*, 2000, **7**, 115.
46. L. Rong, Y. Kojima, S. Koda and H. Nomura, *Ultrason. Sonochem.*, 2001, **8**, 11.
47. Y. Mizukoshi, E. Takagi, H. Okuno, R. Oshima, Y. Maeda and Y. Nagata, *Ultrason. Sonochem.*, 2001, **8**, 1.
48. R. A. Pethrick, *Adv. Sonochem.*, 1991, **2**, 65.
49. H. W. Melville and A. Murray, *Trans. Faraday Soc.*, 1950, **46**, 996.
50. D. R. Bassett and A. E. Hamielec, "Emulsion Polymers and Emulsion Polymerization", A. C. S. Symposium Series 165, American Chemical Society, Washington, 1981.
51. J. P. Lorimer, T. J. Mason, K. Fiddy, D. Kershaw, R. Groves and D. Dodgson, "Ultrasonics International Conference Proceedings", 1989, 1283.
52. J. J. Lebout and H. Porte in "Comprehensive Polymer Science", eds. J. C. Bevington and G. Allen, Pergamon, New York, 1989, Vol. 5, Chap. 34.
53. B. H. Han and P. Boudjouk, *Tetrahedron Lett.*, 1981, **22**, 3813.
54. K. Ivanov, T. Popov and S. Slavov, *Izv. Khim.*, 1987, **20**, 201.
55. T. Popov, D. Klissurski, K. Ivanov and I. Pesheva, *Stud. Sur. Sci. Catal.*, 1987, **31**, 191.
56. R. Ranganathan, I. Mathur, N. N. Backshi and J. F. Mathews, *Ind. Eng. Prod. Res. Develop.*, 1973, **12**, 155.
57. P. Boudjouk in "Ultrasound : Chemical, Physical and Biological Effects", ed. K. S. Suslick, Verlag Chemie International, 1988, Chap. 5.
58. P. Boudjouk and B. Hauck, "XXV Organosilicon Symposium", Los Angeles, 1992, Abstr. no. 82.
59. T. J. Mason, J. P. Lorimer and D. J. Walton, *Ultrasonics*, 1990, **28**, 333.
60. F. J. Del Campo, A. Neudeck, R. G. Compton and F. Marken, *J. Electroanal. Chem.*, 1999, **477**, 71.
61. Y. Masti, M. Homyonfer, A. Gedanken and G. Hodes, *Adv. master. (Weinheim)*, 1999, **11**, 1010.
62. Bioprocessing Technology, Technical Insights, U.S.A., 1989.
63. Nippon Shokubai, Kagaku Kogyo EP 0 249 969 A2/1987.
64. R. Katoh, E. Yanase, H. Yokoi, S. Usuba, Y. Kakudate and S. Fujiwara, *Ultrason. Sonochem.*, 1998, **5**, 37.
65. C. Petrier and A. Francony, *Wat. Sci. Tech.*, 1997, **35**, 175.