GREEN CHEMISTRY

Laurea Magistrale in Scienze Chimiche

Prof. Leucio Rossi

6 CFU – AA 2017-2018

Green Chemistry 11

GREEN TECHNIQUES FOR ORGANIC SYNTHESIS III

Green Chemistry – Prof. Rossi – AA 2017-2018

ULTRASOUND TECHNOLOGY IN GREEN CHEMISTRY

INTRODUCTION

Introduction

Ultrasound refers to inaudible sound waves with frequencies in the range of 16 KHz–500 MHz, above the upper limit of human hearing.

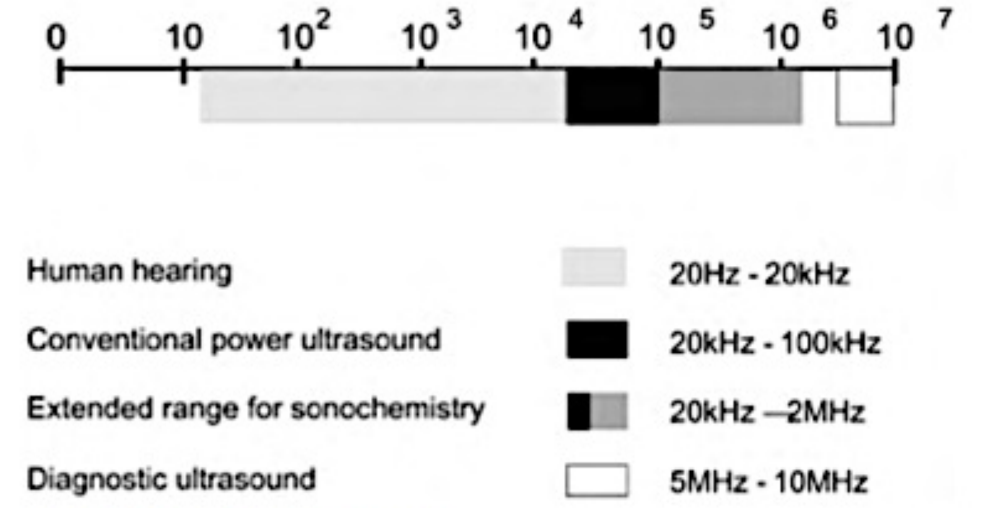
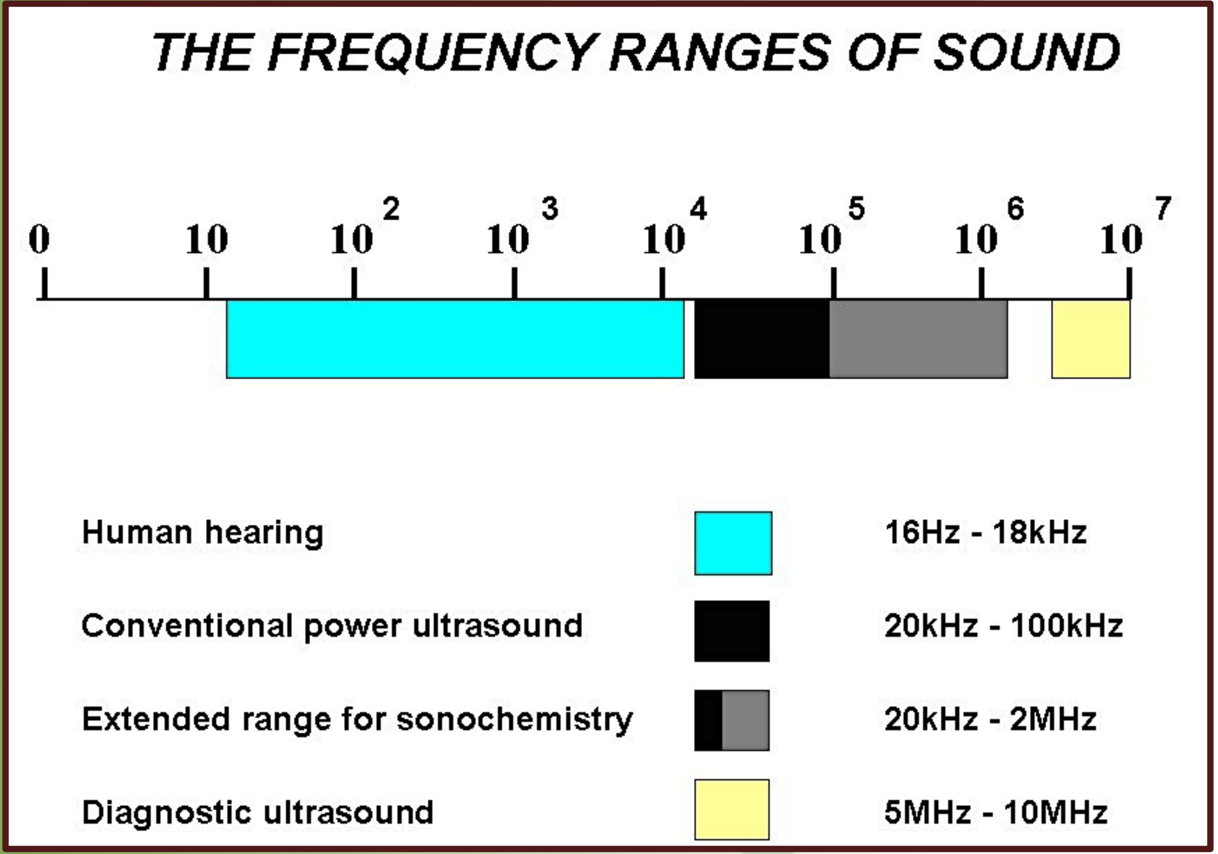


Fig. 1.1. Sound frequency ranges.

Introduction

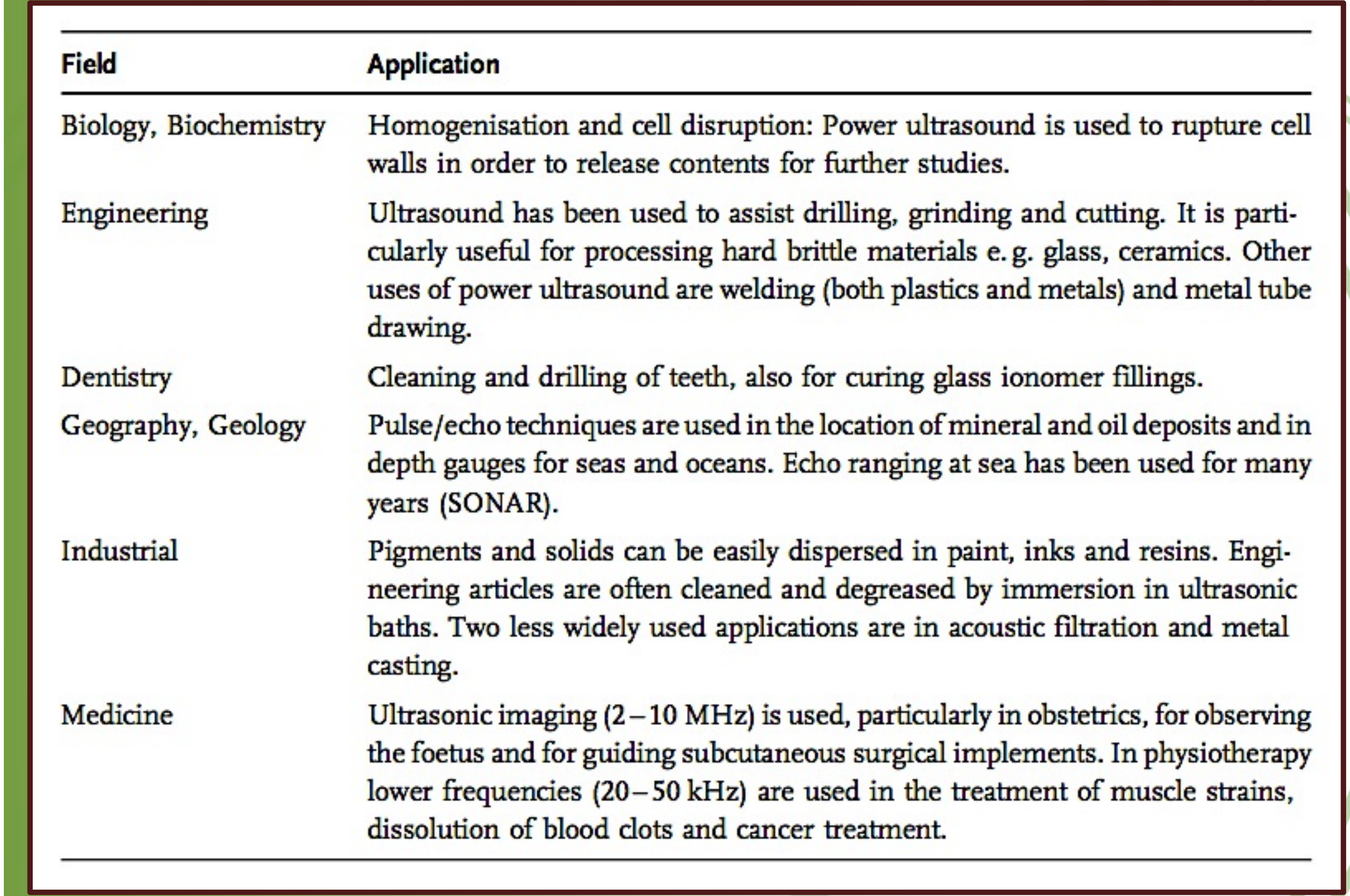
Sound consists of pressure waves transmitted through a medium (gas, liquid or solid) as cycles of compression and expansion



THE FREQUENCY RANGES OF SOUND

Human hearing	🟦	16Hz - 18kHz
Conventional power ultrasound	⬛	20kHz - 100kHz
Extended range for sonochemistry	⬛▨	20kHz - 2MHz
Diagnostic ultrasound	🟨	5MHz - 10MHz

Introduction



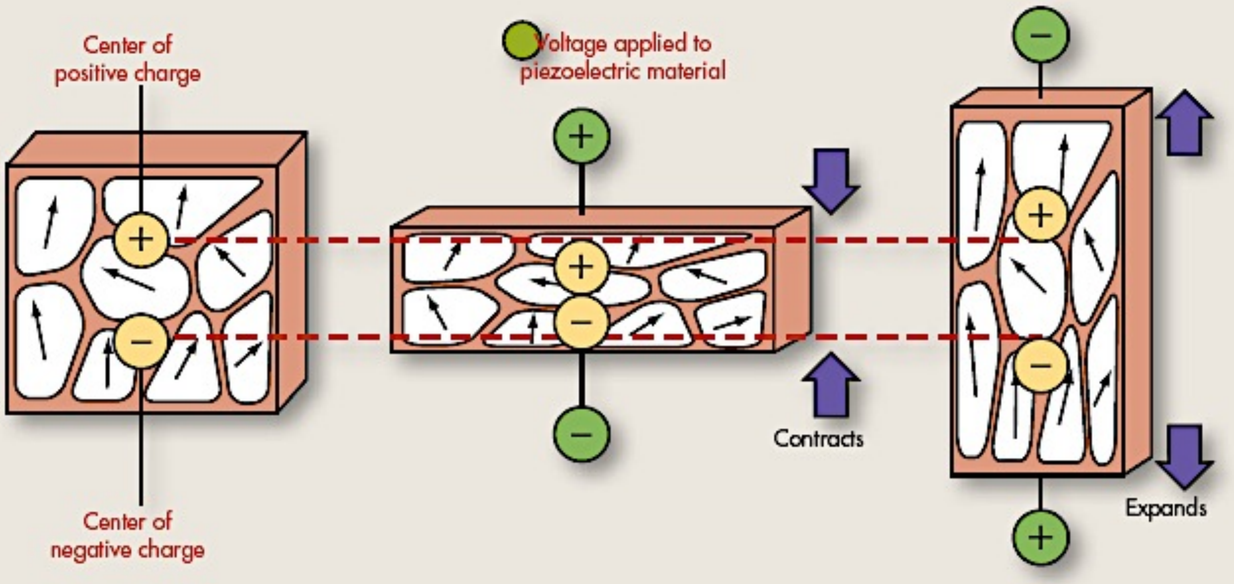
Field	Application
Biology, Biochemistry	Homogenisation and cell disruption: Power ultrasound is used to rupture cell walls in order to release contents for further studies.
Engineering	Ultrasound has been used to assist drilling, grinding and cutting. It is particularly useful for processing hard brittle materials e. g. glass, ceramics. Other uses of power ultrasound are welding (both plastics and metals) and metal tube drawing.
Dentistry	Cleaning and drilling of teeth, also for curing glass ionomer fillings.
Geography, Geology	Pulse/echo techniques are used in the location of mineral and oil deposits and in depth gauges for seas and oceans. Echo ranging at sea has been used for many years (SONAR).
Industrial	Pigments and solids can be easily dispersed in paint, inks and resins. Engineering articles are often cleaned and degreased by immersion in ultrasonic baths. Two less widely used applications are in acoustic filtration and metal casting.
Medicine	Ultrasonic imaging (2–10 MHz) is used, particularly in obstetrics, for observing the foetus and for guiding subcutaneous surgical implements. In physiotherapy lower frequencies (20–50 kHz) are used in the treatment of muscle strains, dissolution of blood clots and cancer treatment.

Introduction

- The use of ultrasound to promote chemical reactions is called **sonochemistry**.
- The effects of ultrasound observed during organic reactions are due to **cavitation**, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid.
- Cavitation induces very high local temperatures and pressures inside the bubbles (cavities), leading to turbulent flow of the liquid and enhanced mass transfer.

Introduction

Piezoelectric Effect (Pierre and Jacques Curie 1880)



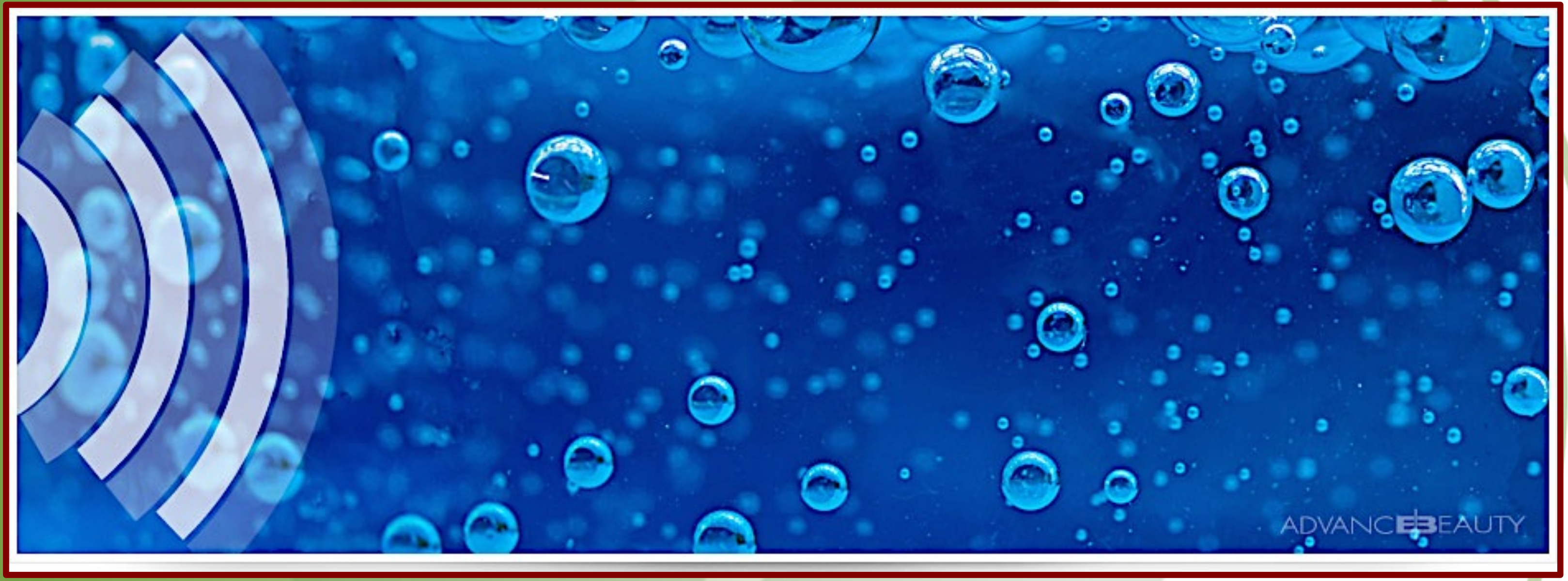
1. The piezoelectric effect causes crystal materials like quartz to generate an electric charge when the crystal material is compressed, twisted, or pulled. The reverse also is true, as the crystal material compresses or expands when an electric voltage is applied.

Introduction

Piezoelectric Effect (Pierre and Jacques Curie 1880)

Piezoelectric materials respond to the application of an electrical potential across opposite faces with a small change in dimension.
If the potential is alternated at high frequencies, the crystal converts the electrical energy to mechanical vibration energy; at sufficiently high alternating potential, high frequency sound (ultrasound) is generated.

Cavitation



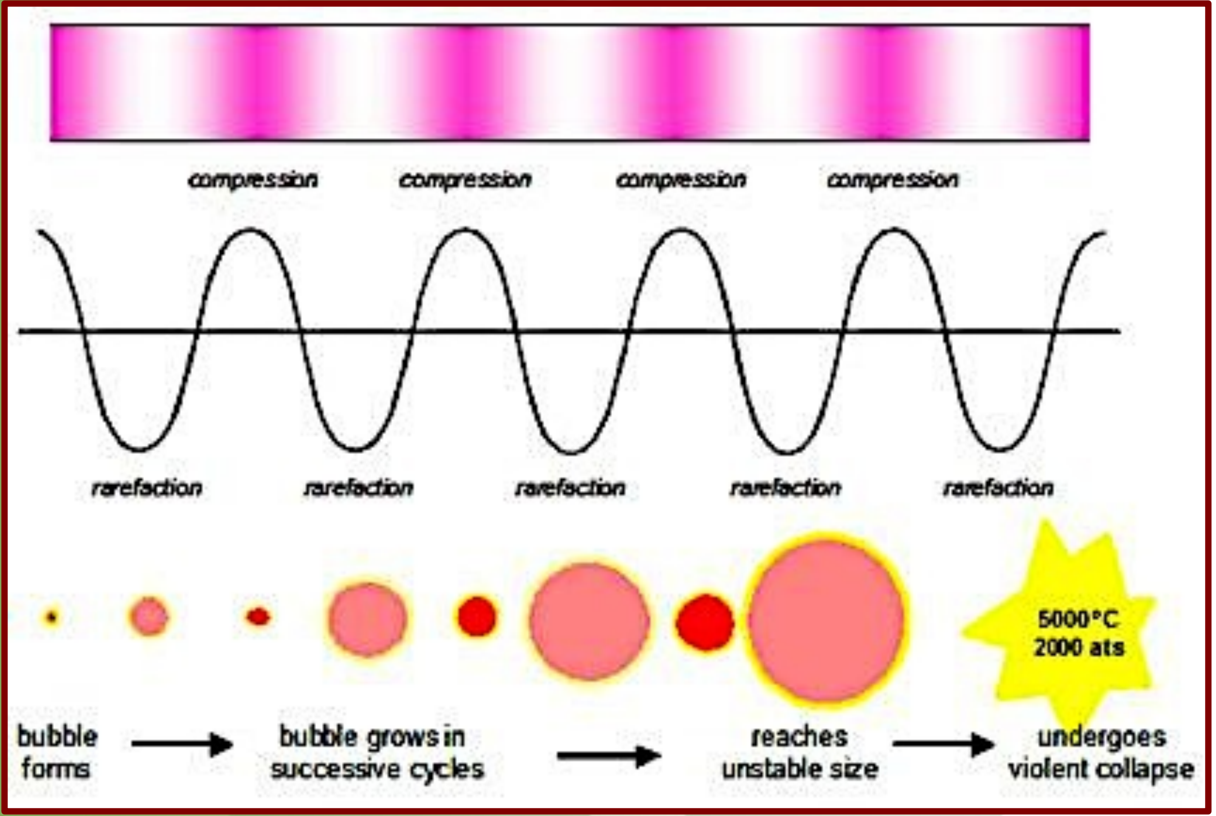
Cavitation

- Since ultrasound (waves of compression and expansion) is generated by a piezoelectric ceramic in a probe or cleaning bath, it will pass through a liquid, with the expansion cycles exerting negative pressure on the liquid.
- If this applied negative pressure is strong enough to break down the intermolecular van der Waals force of the liquid, small cavities or gas-filled microbubbles are formed.

Cavitation

- Cavitation is considered to be a nucleated process, meaning that these micrometer-scale bubbles will be formed at pre-existing weak points in the liquid, such as gas-filled crevices in suspended particulate matter or transient microbubbles from prior cavitation events.
- Most liquids are sufficiently contaminated by small particles that cavitation can be readily initiated at moderate negative pressures.

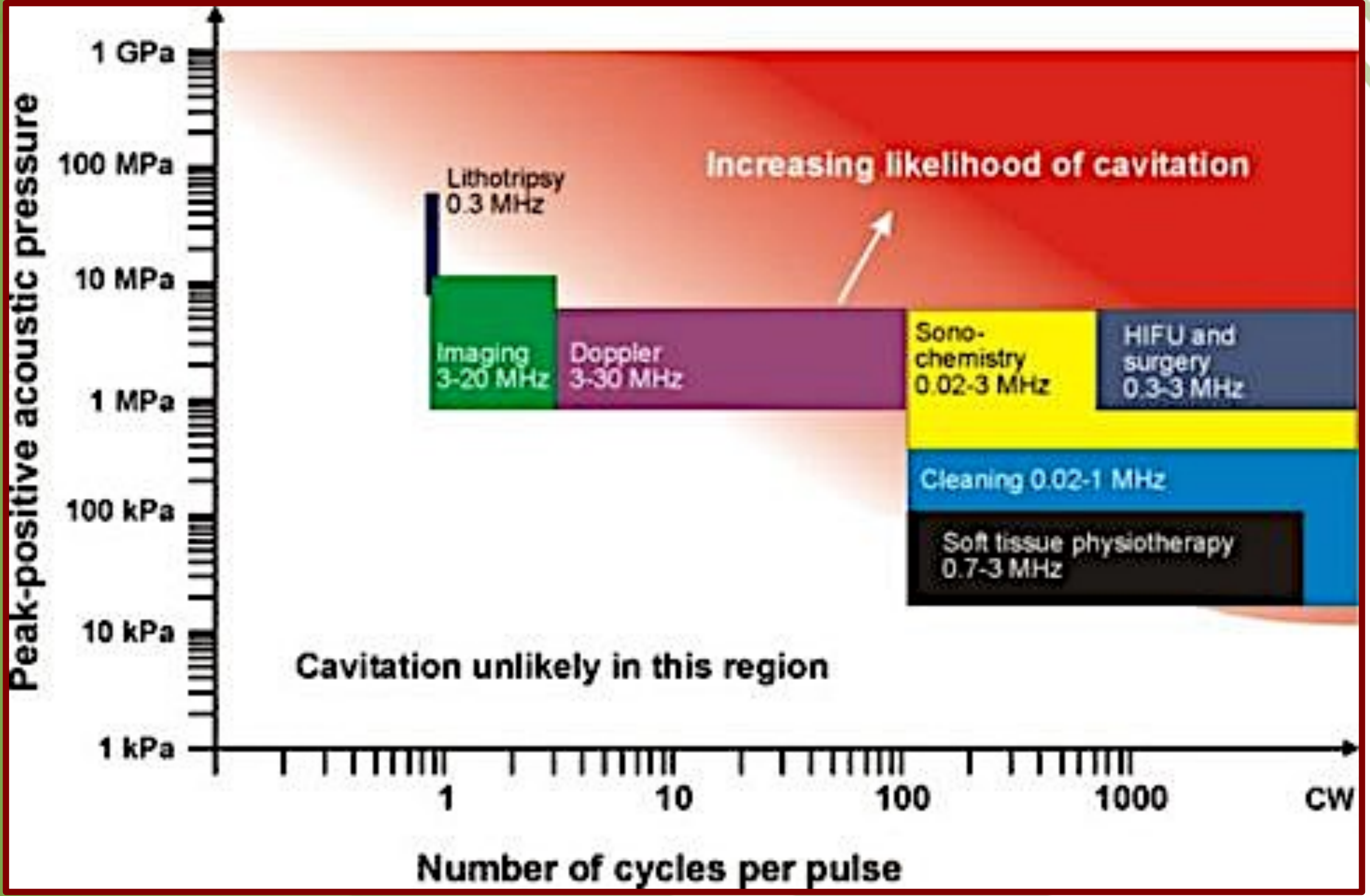
Cavitation


compression
compression
compression
compression
rarefaction
rarefaction
rarefaction
rarefaction
rarefaction
5000°C
2000 ats
bubble forms
bubble grows in successive cycles
reaches unstable size
undergoes violent collapse

Cavitation

- As microbubbles are formed, they absorb energy from ultrasound waves and grow.
- However, it will reach a stage where they can no longer absorb energy as efficiently.
- Without the energy input, the cavity can no longer sustain itself and implodes.
- It is this implosion of the cavity that creates an unusual environment for chemical reactions

Cavitation


Peak-positive acoustic pressure
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
Lithotripsy 0.3 MHz
Increasing likelihood of cavitation
Imaging 3-20 MHz
Doppler 3-30 MHz
Sono-chemistry 0.02-3 MHz
HIFU and surgery 0.3-3 MHz
Cleaning 0.02-1 MHz
Soft tissue physiotherapy 0.7-3 MHz
Cavitation unlikely in this region
1
10
100
1000
CW
Number of cycles per pulse

Cavitation

When a pressure wave of sufficient intensity propagates through a liquid, formation of vapor bubbles may occur. Such cavities result when a negative pressure exceeds the tensile strength of the liquid, which is the maximum stress that a substance can withstand from stretching without tearing.

Cavitation

There are a few factors that can affect the efficiency of bubble collapse, such as:

(1) vapor pressure;

(2) temperature;

(3) thermal conductivity;

(4) surface tension and viscosity;

(5) the ultrasound frequency;

(6) acoustic intensity.

Cavitation

as the frequency increases the production of cavitation bubbles becomes more difficult to achieve in the available time

greater sound intensities (i. e. greater amplitudes) will need to be employed, over these shorter periods, to ensure that the cohesive forces of the liquid are overcome.

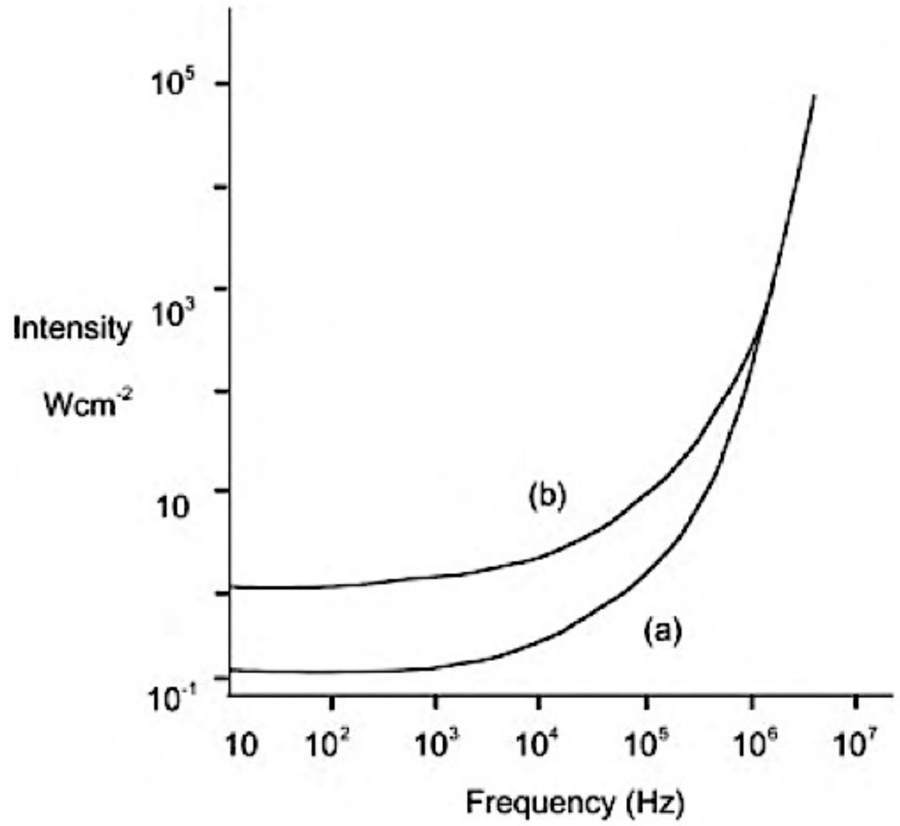
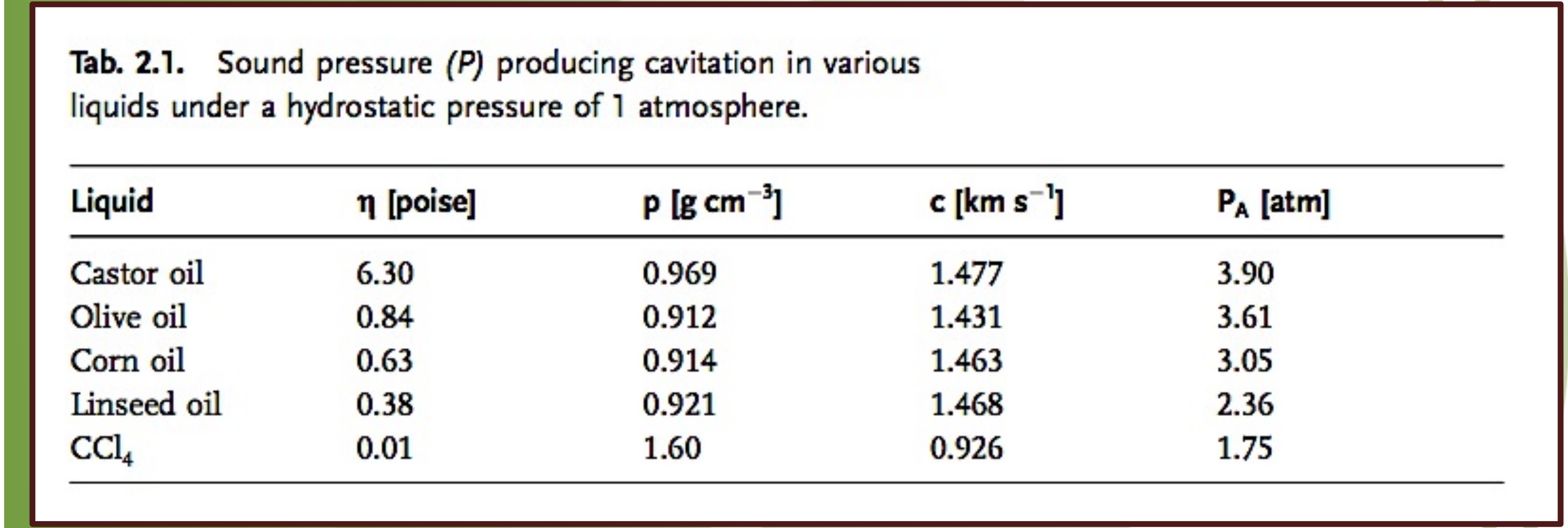


Fig. 2.11. Variation in threshold intensity with frequency; (a) aerated water; (b) air free water.

Cavitation



Tab. 2.1. Sound pressure *(P)* producing cavitation in various liquids under a hydrostatic pressure of 1 atmosphere.

Liquid	η [poise]	p [g cm^{-3}]	c [km s^{-1}]	P_A [atm]
Castor oil	6.30	0.969	1.477	3.90
Olive oil	0.84	0.912	1.431	3.61
Corn oil	0.63	0.914	1.463	3.05
Linseed oil	0.38	0.921	1.468	2.36
CCl_4	0.01	1.60	0.926	1.75

Cavitation

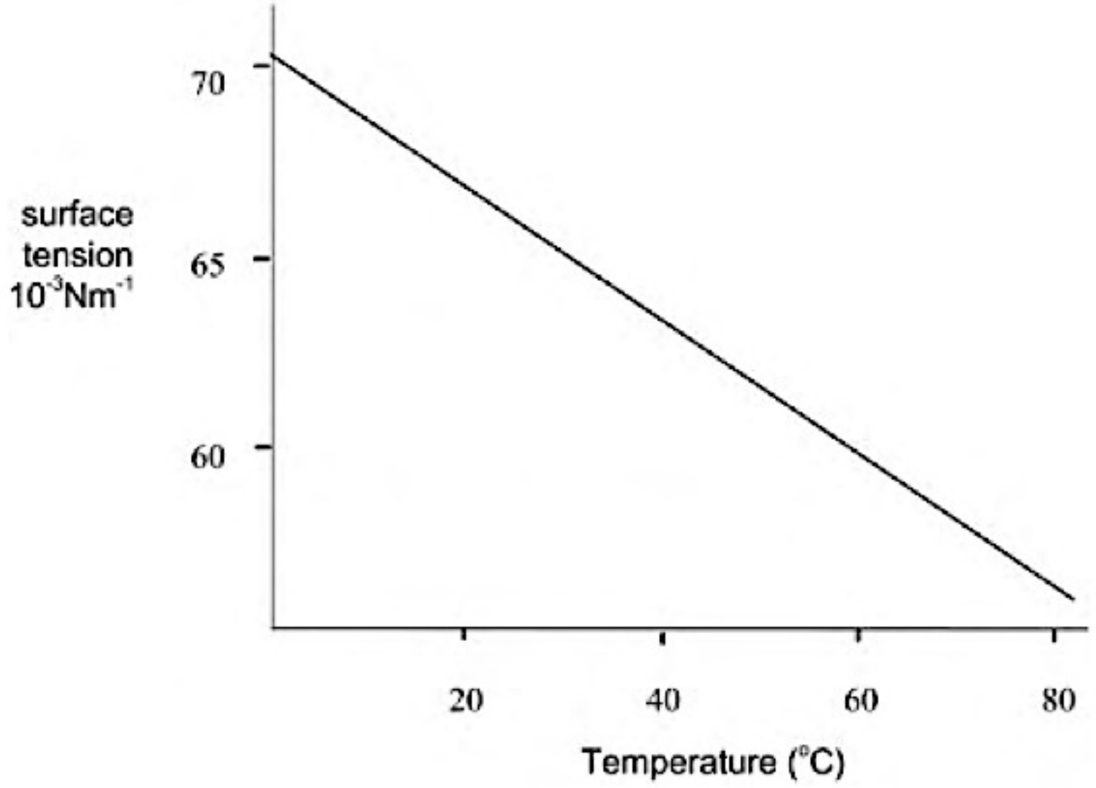


Fig. 2.13. Variation of the surface tension of water with temperature.

Cavitation

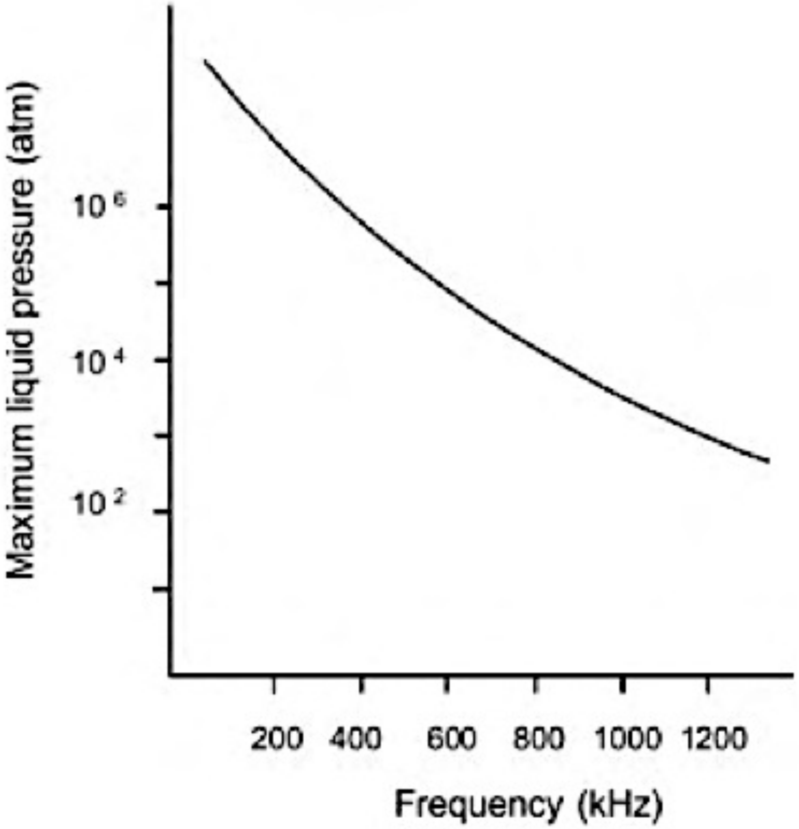


Fig. 2.24. Variation with frequency of maximum fluid pressure during collapse; $R_e = 3.2 \times 10^{-4}$ cm; $P_A = 4$ atm.

Cavitation

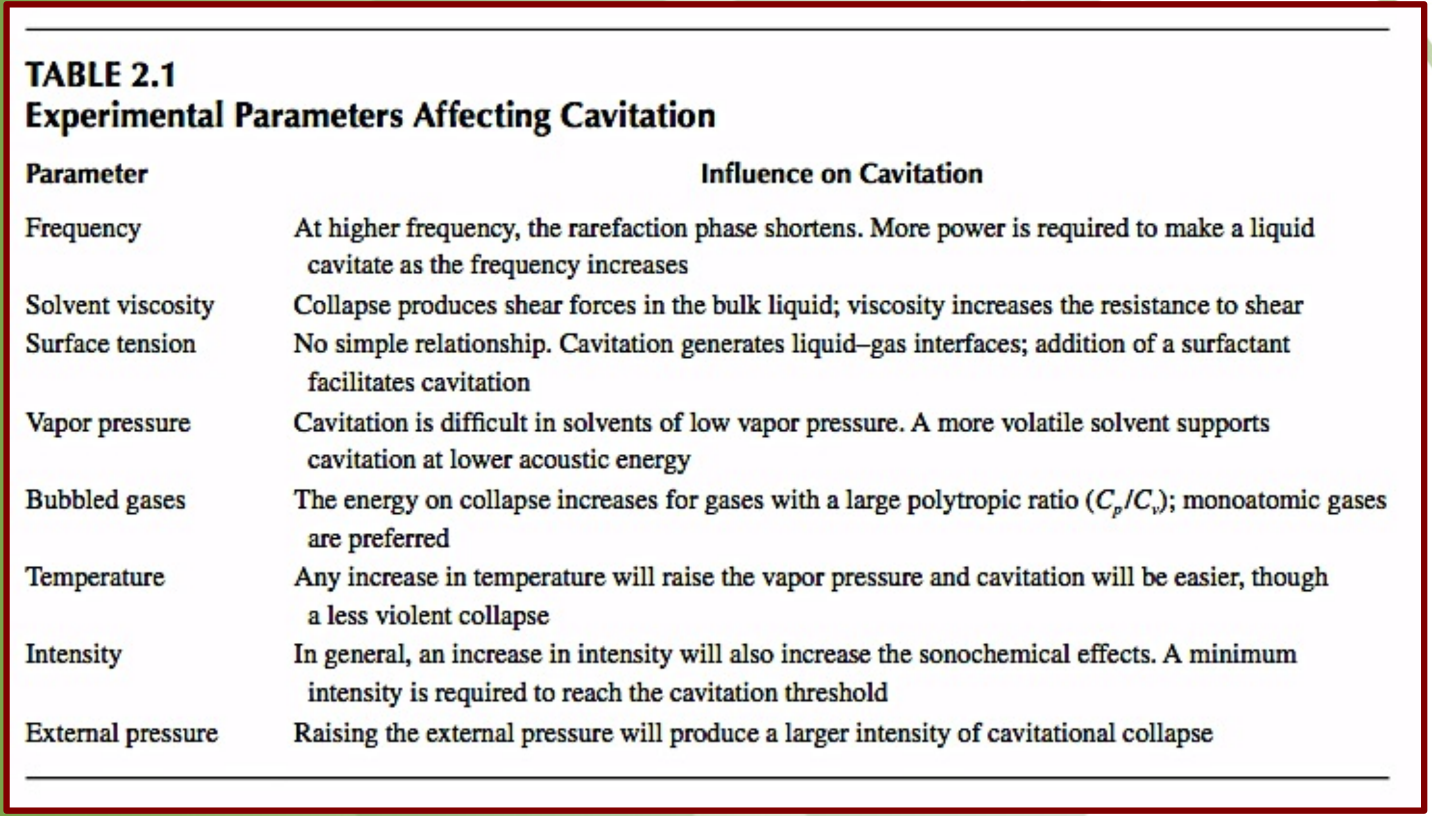


TABLE 2.1
Experimental Parameters Affecting Cavitation

Parameter	Influence on Cavitation
Frequency	At higher frequency, the rarefaction phase shortens. More power is required to make a liquid cavitate as the frequency increases
Solvent viscosity	Collapse produces shear forces in the bulk liquid; viscosity increases the resistance to shear
Surface tension	No simple relationship. Cavitation generates liquid–gas interfaces; addition of a surfactant facilitates cavitation
Vapor pressure	Cavitation is difficult in solvents of low vapor pressure. A more volatile solvent supports cavitation at lower acoustic energy
Bubbled gases	The energy on collapse increases for gases with a large polytropic ratio (C_p/C_v); monoatomic gases are preferred
Temperature	Any increase in temperature will raise the vapor pressure and cavitation will be easier, though a less violent collapse
Intensity	In general, an increase in intensity will also increase the sonochemical effects. A minimum intensity is required to reach the cavitation threshold
External pressure	Raising the external pressure will produce a larger intensity of cavitational collapse

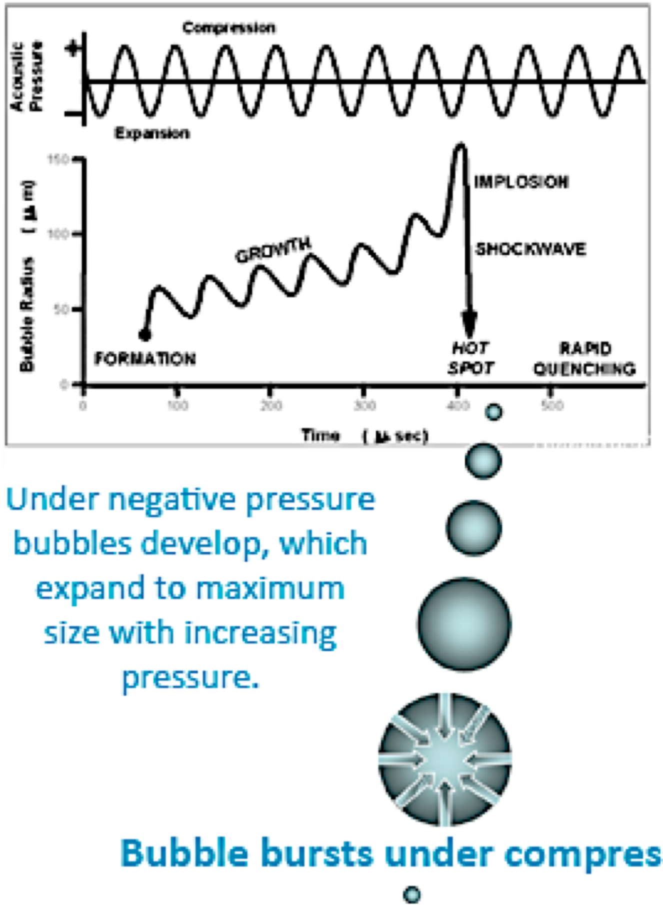
Cavitation

Since the wavelength of ultrasound between successive compression waves measures approximately from 10 to 10^{-3} cm, it does not directly interact with molecules to induce chemical change.

Basically, two theories have been proposed to explain the effect of cavitation on chemical reactions: the “hot spot” and electrical microdischarge theories.

Cavitation

The "hot spot" theory relies on bubble collapse in the liquid to produce enormous amounts of energy from conversion of the kinetic energy of liquid motion into heating of the bubble contents.



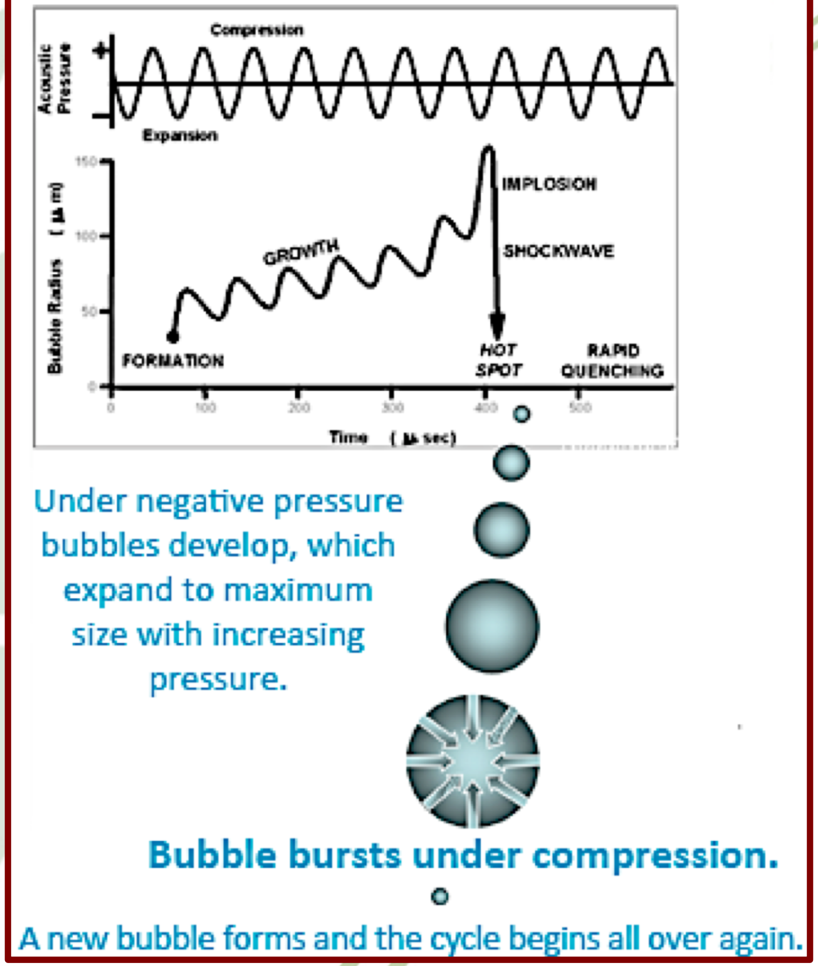
Under negative pressure bubbles develop, which expand to maximum size with increasing pressure.

Bubble bursts under compression.

A new bubble forms and the cycle begins all over again.

Cavitation

Compression of the bubbles during cavitation is more rapid than thermal transport, resulting in the generation of short-lived localized hot spots. Experimental results have shown that these bubbles have temperatures around 5000 K, pressures of approximately 1000 atm, and heating and cooling rates above 1010 K/s.



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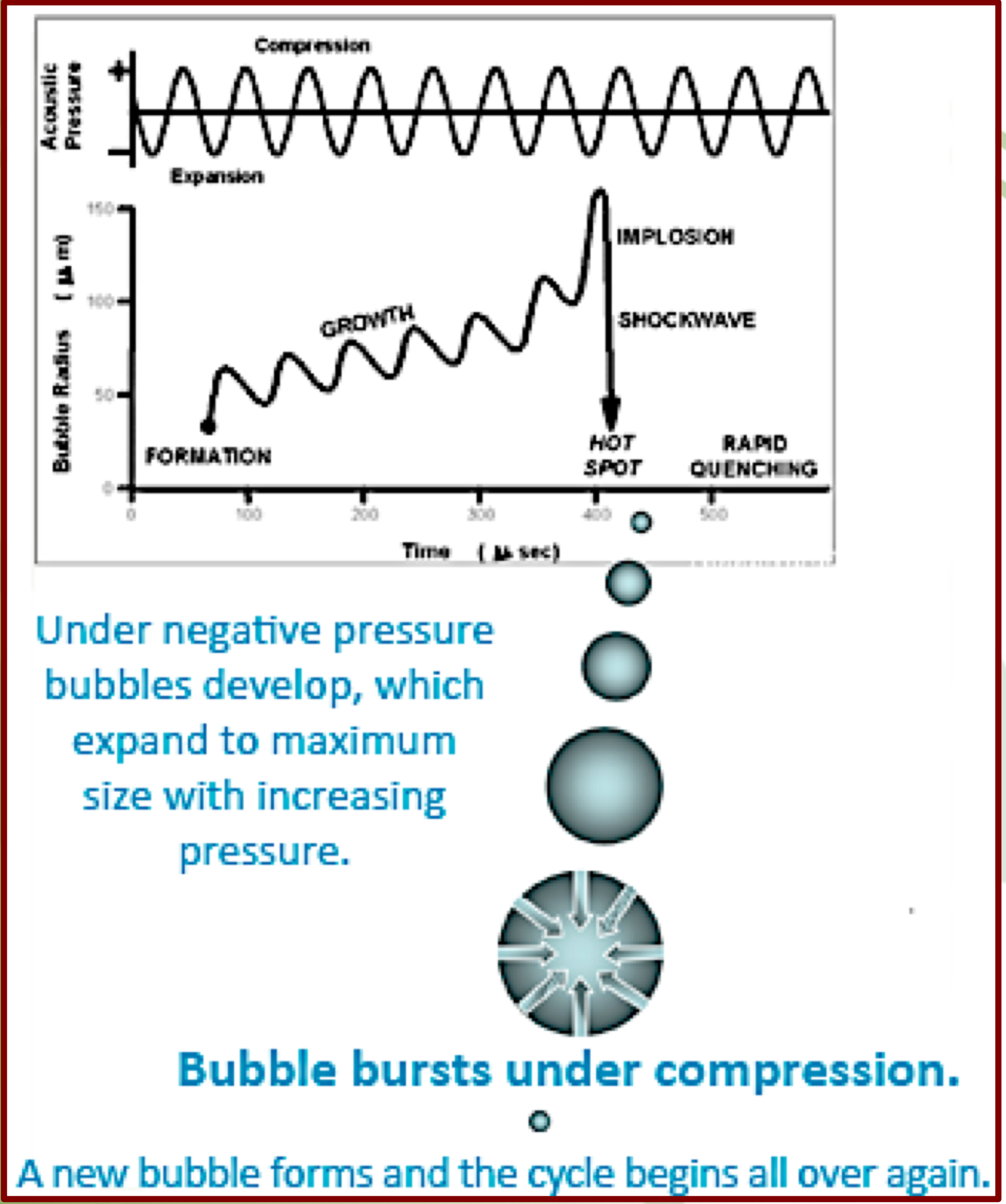
Cavitation



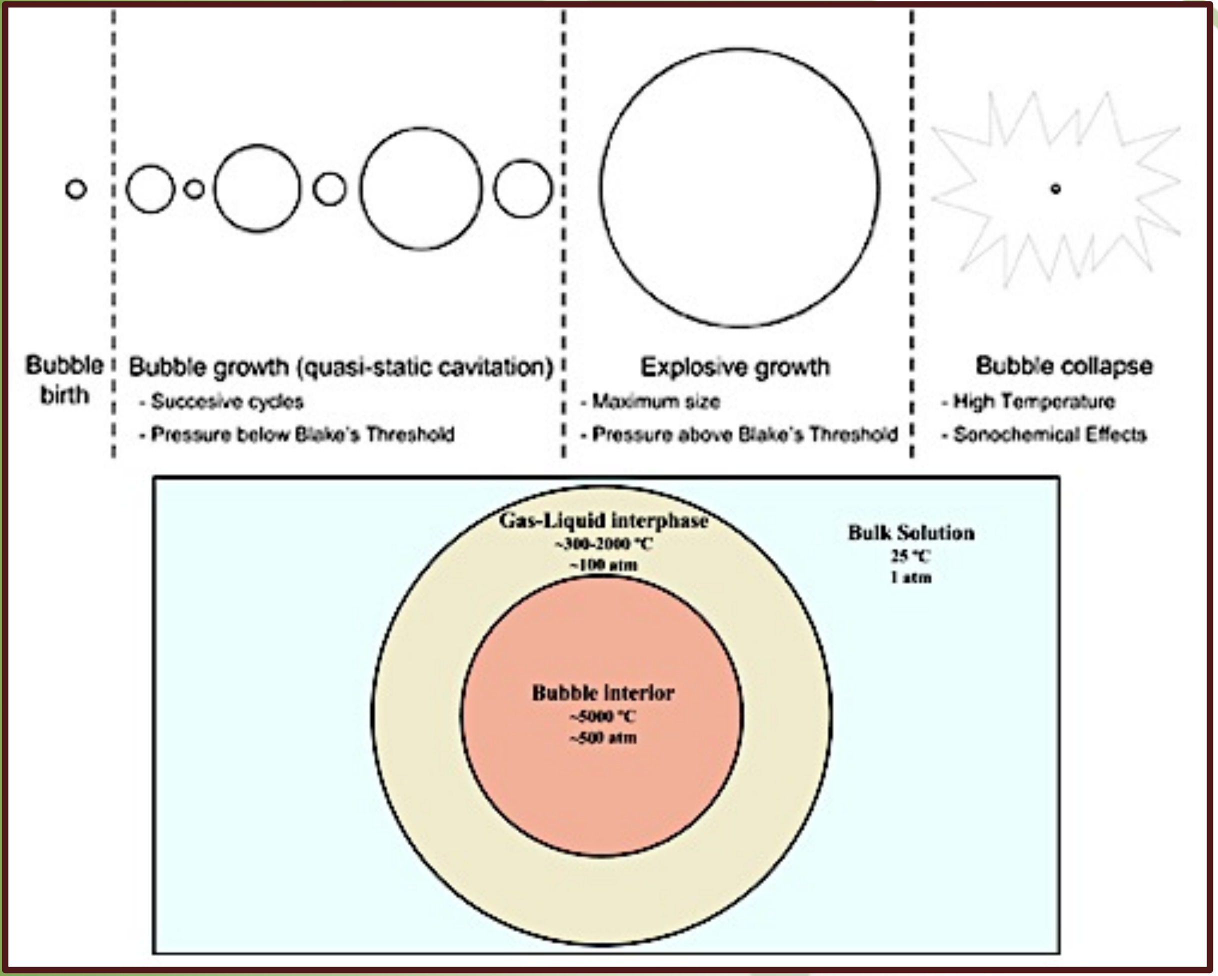
Under negative pressure bubbles develop, which expand to maximum size with increasing pressure.

Bubble bursts under compression.

A new bubble forms and the cycle begins all over again.

Cavitation

Hot-spot model



Cavitation

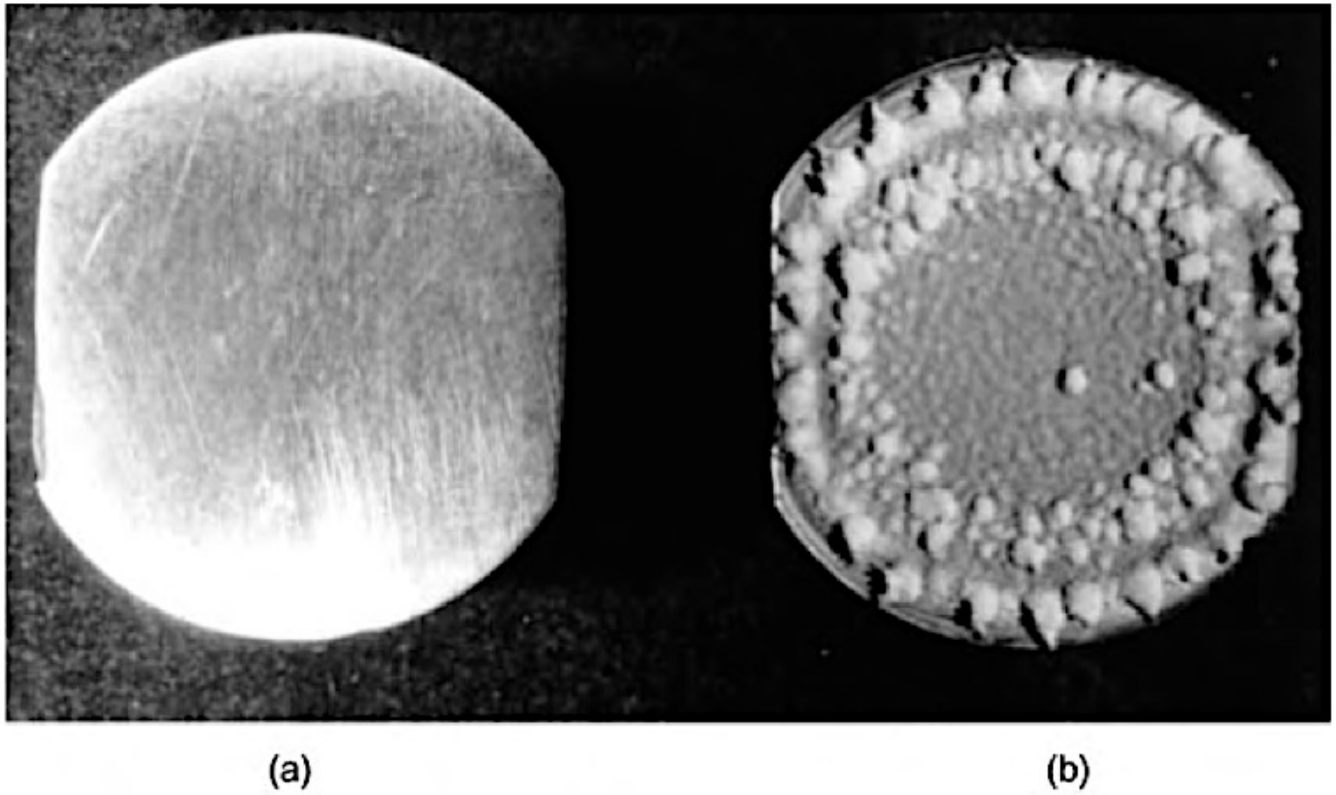

(a) (b)

Fig. 2.9. Erosion of 1 cm diameter tip; (a) initial surface; (b) eroded surface (20 h at 20 W cm^{-2} in benzene).

Cavitation

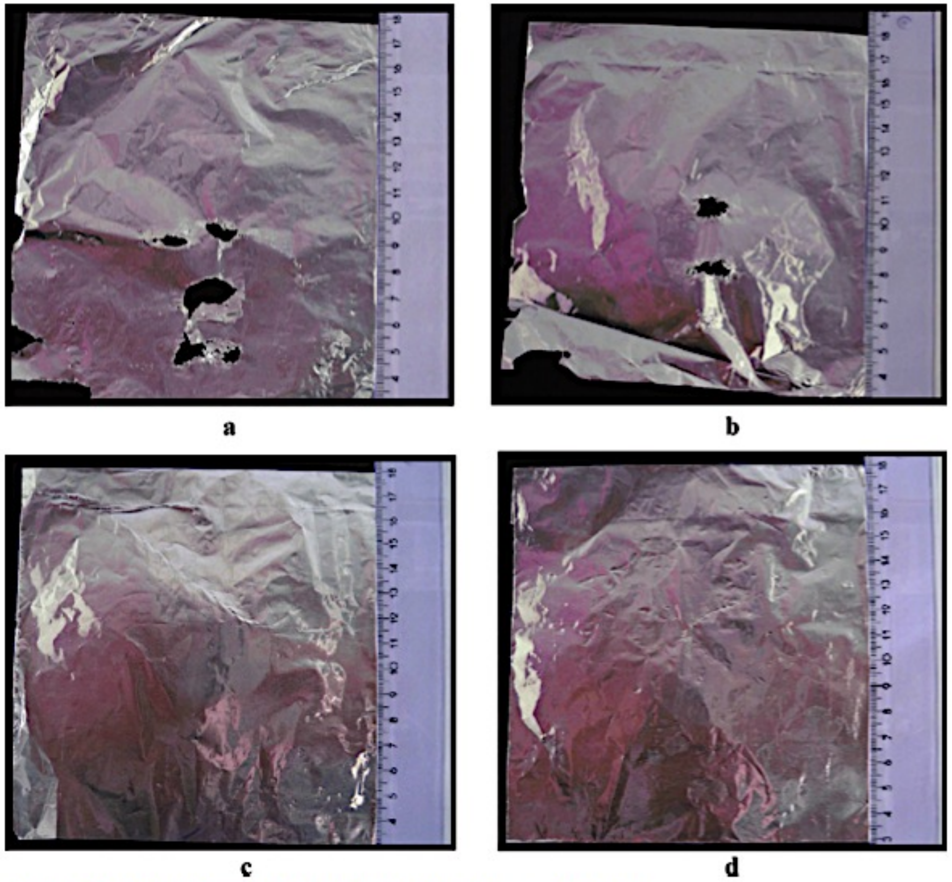


Figure 1.5 Aluminium foil test. Sonication time used for all experiments: 5 min. (a) 35 kHz sonication frequency and 100% sonication amplitude; (b) 35 kHz sonication frequency and 50% sonication amplitude; (c) 130 kHz sonication frequency and 100% sonication amplitude; and (d) 130 kHz sonication frequency and 50% sonication amplitude.

Introduction

Although the use of ultrasound as the primary means of stimulating chemical reactions and processes has been known for many years, this safe form of irradiation has become increasingly popular during the last two decades along with the emergence of other stimulating techniques (e.g., microwaves, photochemistry, electrochemistry, or high pressure) in the search for more environmentally benign conditions.

Sonochemistry

As the frequency is increased cavitation bubble lifetime and collapse energy are reduced.

At high frequency (> 3 MHz) there is not enough time during the rarefaction cycle for bubble growth to achieve sufficient size to disrupt the liquid.

For cavitation at high frequency more power is needed since more energy is lost to molecular motion of the liquid. It is for this reason that most commercially available pieces of ultrasonic equipment used in sonochemistry operates at the lower end of the ultrasonic range (20±50kHz).

Higher frequencies are advantageous when radical production is important.

Sonochemistry

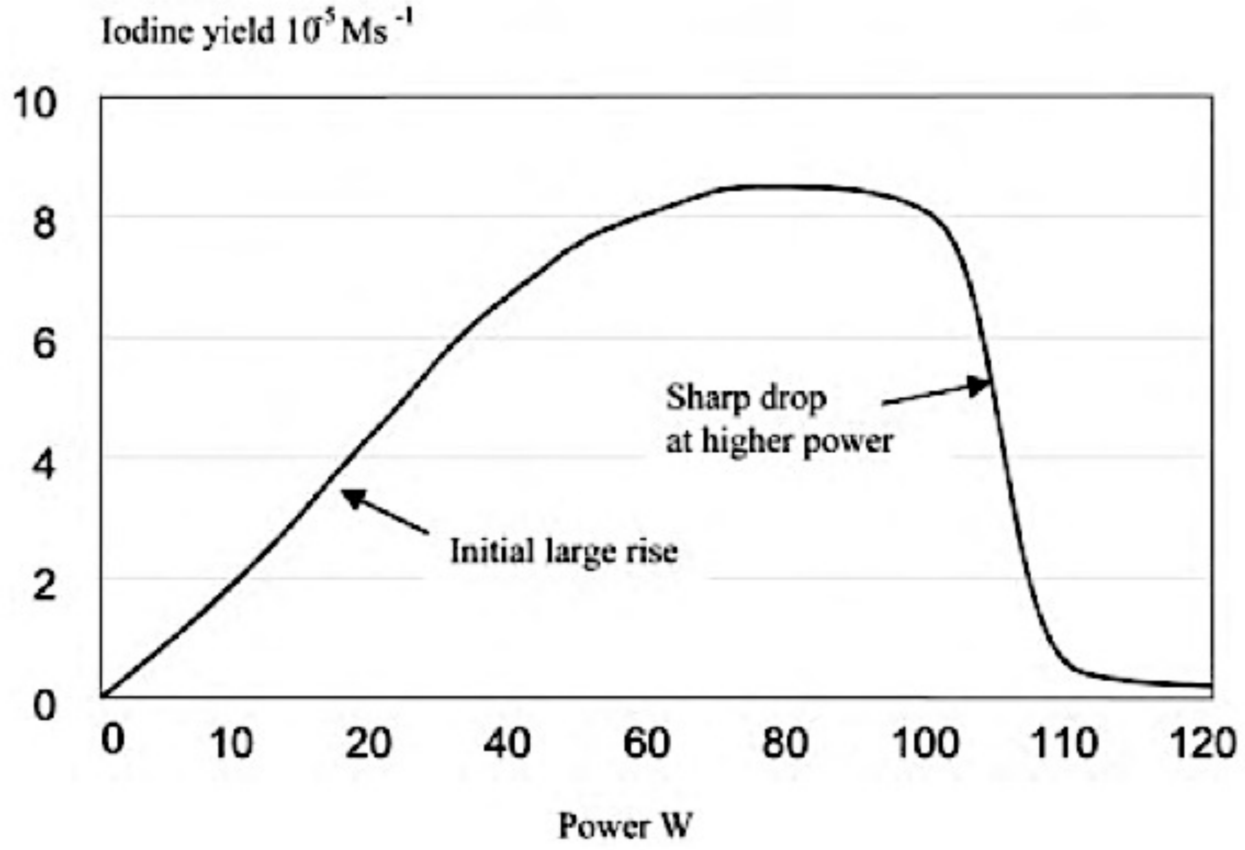


Fig. 3.1. Effect of increasing power on a sonochemical reaction.

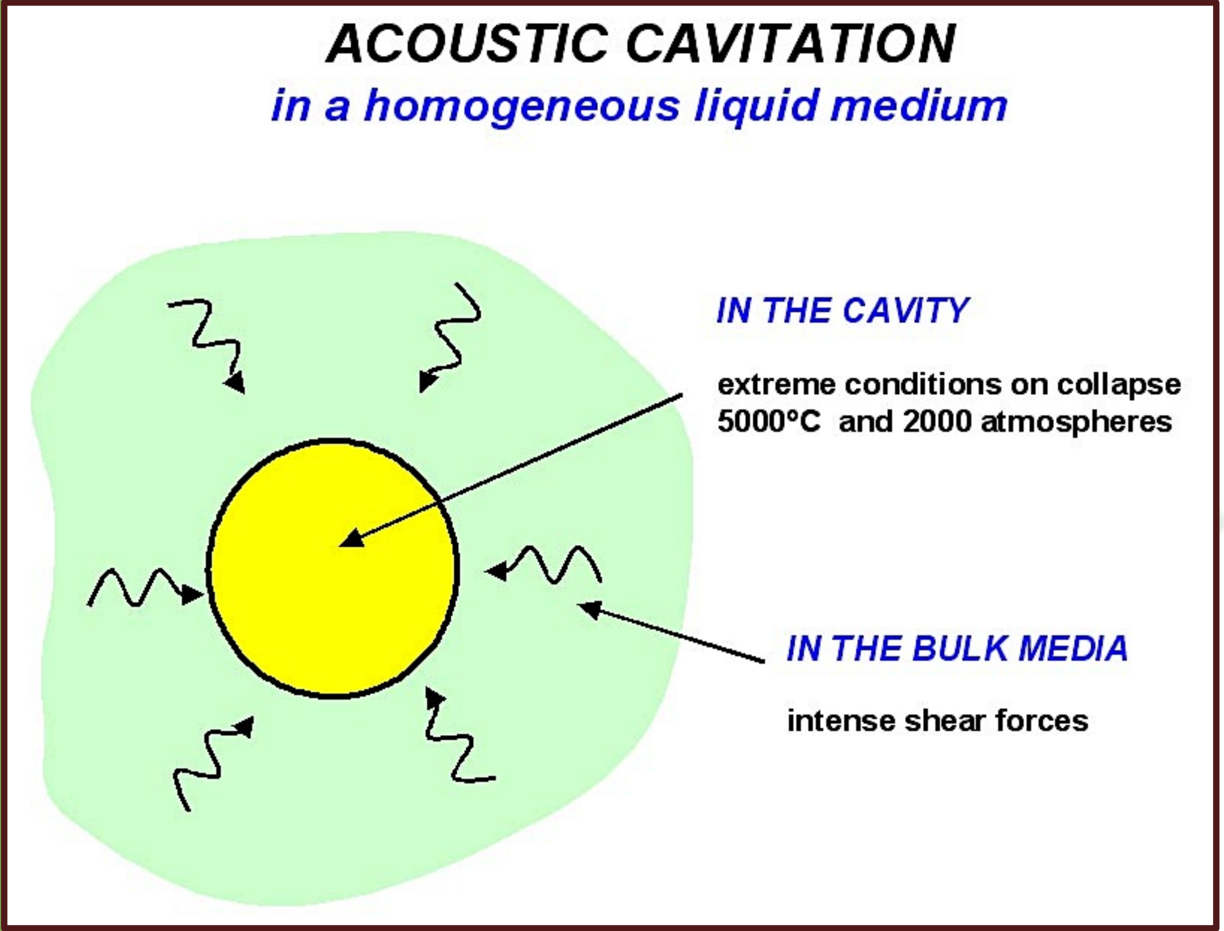
Sonochemistry

Three classes of sonochemical reactions exist:

- **Homogeneous Sonochemistry**
- **Heterogeneous Sonochemistry (Liquid–Liquid or Solid–Liquid Systems)**
- **Sonocatalysis (Overlap Homogeneous and Heterogeneous Sonochemistry)**

Sonochemistry

Homogeneous Sonochemistry



Sonochemistry

Homogeneous Sonochemistry

- **proceed via radical or radical-ion intermediates. sonication is able to affect reactions proceeding through radicals**
- **it is unlikely to affect ionic reactions**

In the case of volatile molecules, the bubbles (or cavities) are believed to act as a microreactor; as the volatile molecules enter the microbubbles and the high temperature and pressure produced during cavitation break their chemical bonds, short-lived chemical species are returned to the bulk liquid at room temperature, thus reacting with other species.

Sonochemistry

Homogeneous Sonochemistry

- **proceed via radical or radical-ion intermediates**
- **sonication is able to affect reactions proceeding through radicals**
- **it is unlikely to affect ionic reactions**

Compounds of low volatility, which are unlikely to enter bubbles and thus be directly exposed to these extreme conditions, still experience a high energy environment resulting from the pressure changes associated with the propagation of the acoustic wave or with bubble collapse (shock waves); alternatively, they can react with radical species generated by sonolysis of the solvent.

Sonochemistry

Heterogeneous Sonochemistry

- proceed via ionic intermediates.
- the reaction is influenced primarily through the mechanical effects of cavitation, such as surface cleaning, particle size reduction, and improved mass transfer.

When cavitation occurs in a liquid near a solid surface, the dynamics of cavity collapse change dramatically. In homogeneous systems, the cavity remains spherical during collapse because its sur-roundings are uniform

Sonochemistry

Heterogeneous Sonochemistry

- proceed via ionic intermediates.
- the reaction is influenced primarily through the mechanical effects of cavitation, such as surface cleaning, particle size reduction, and improved mass transfer.

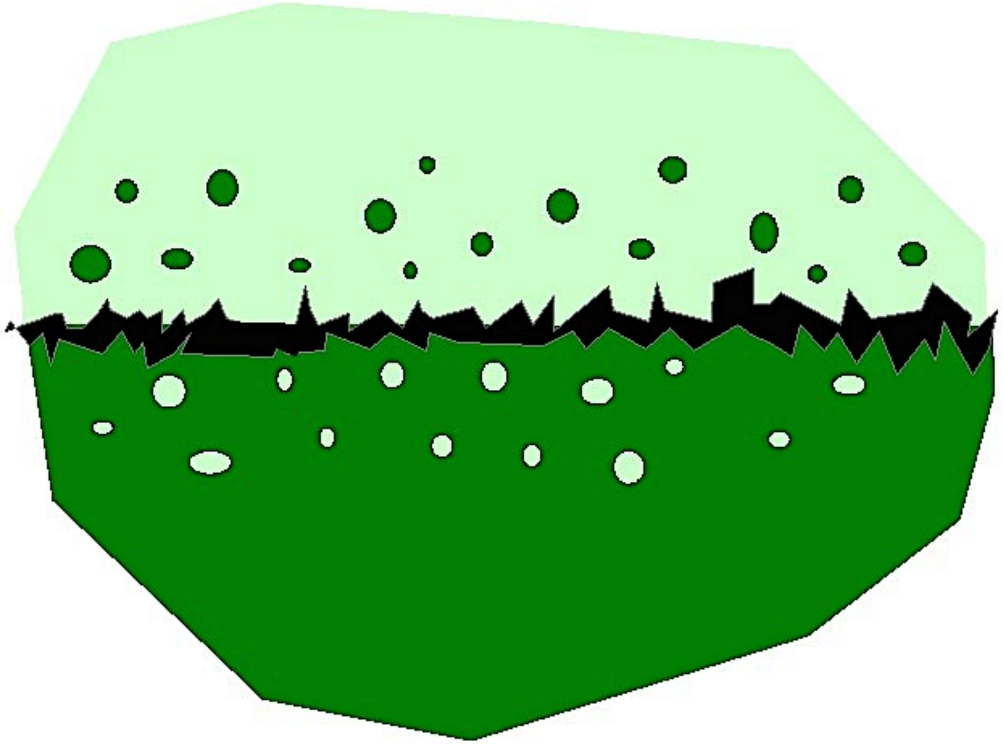
Close to a solid boundary, cavity collapse is very asymmetric and generates high-speed jets of liquid (with velocities of approximately 400 km/h. These jets hit the surface with tremendous force. This process can cause serious damage at the point of impact and produce newly exposed highly reactive surfaces.

Sonochemistry

Heterogeneous Sonochemistry

ACOUSTIC CAVITATION

Heterogeneous liquid / liquid system



powerful
disruption of
phase boundary

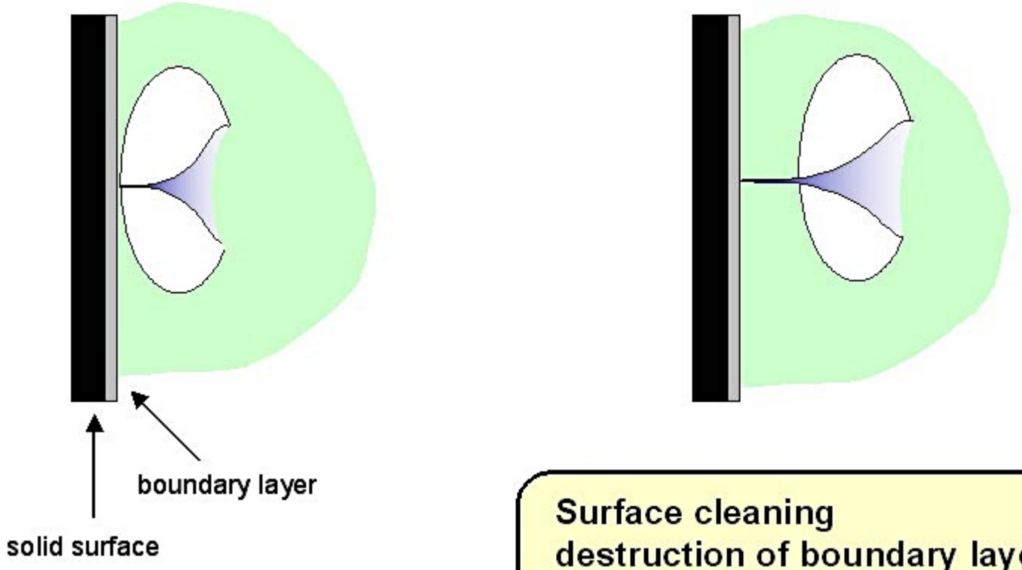
Sonochemistry

Heterogeneous Sonochemistry

ACOUSTIC CAVITATION

Collapse at or near a solid surface

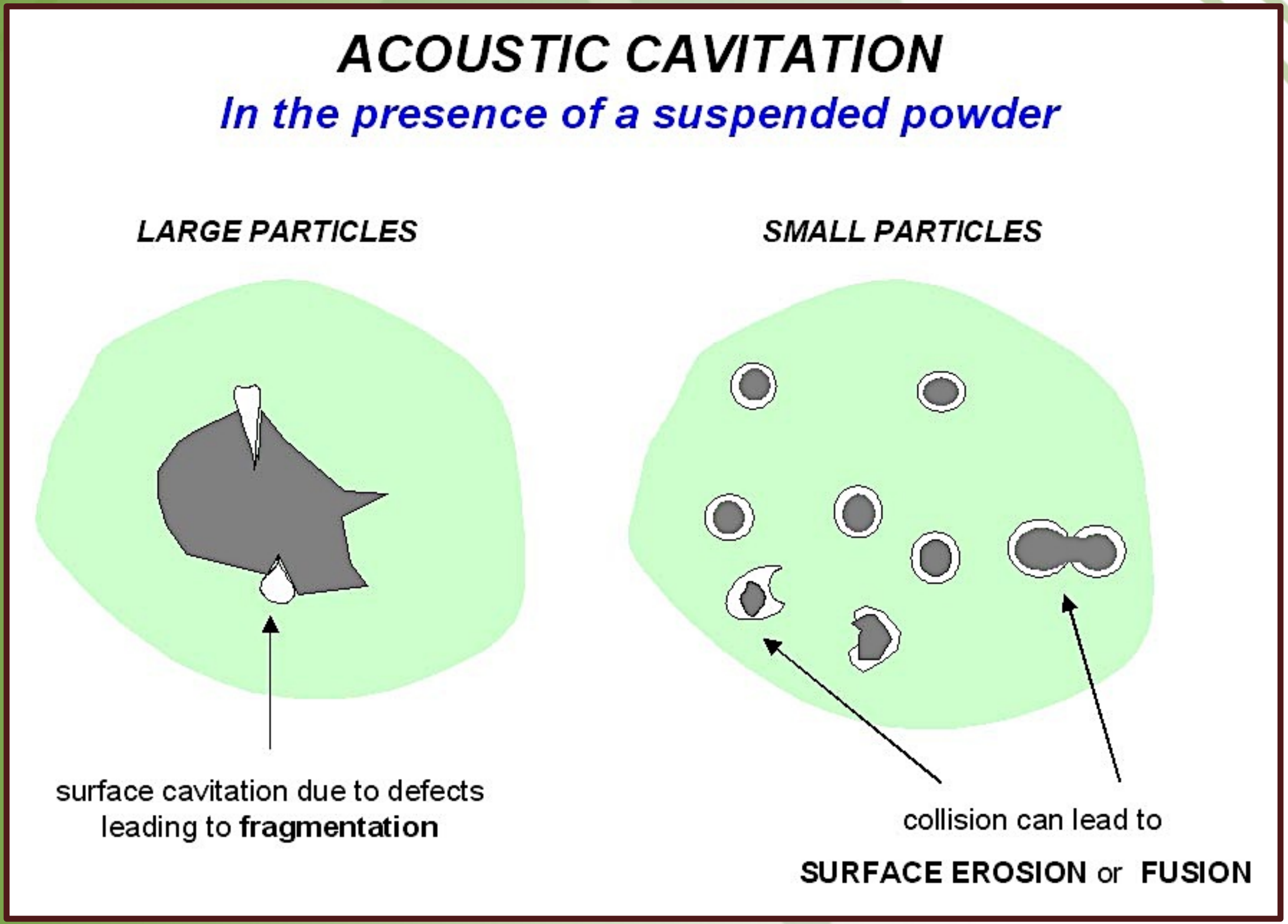
Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface



Surface cleaning
destruction of boundary layer
surface activation
improved mass and heat transfer

Sonochemistry

Heterogeneous Sonochemistry



ACOUSTIC CAVITATION

In the presence of a suspended powder

LARGE PARTICLES

surface cavitation due to defects
leading to **fragmentation**

SMALL PARTICLES

collision can lead to
SURFACE EROSION or **FUSION**

Sonochemistry

Sonocatalysis

heterogeneous reactions that include a radical and ionic mechanism.

Radical reactions will be chemically enhanced by sonication, but the general mechanical effect described above may very well still apply.

If radical and ionic mechanisms lead to different products, ultrasound should favor the radical pathway, potentially leading to a change in the nature of the reaction products.

Equipments

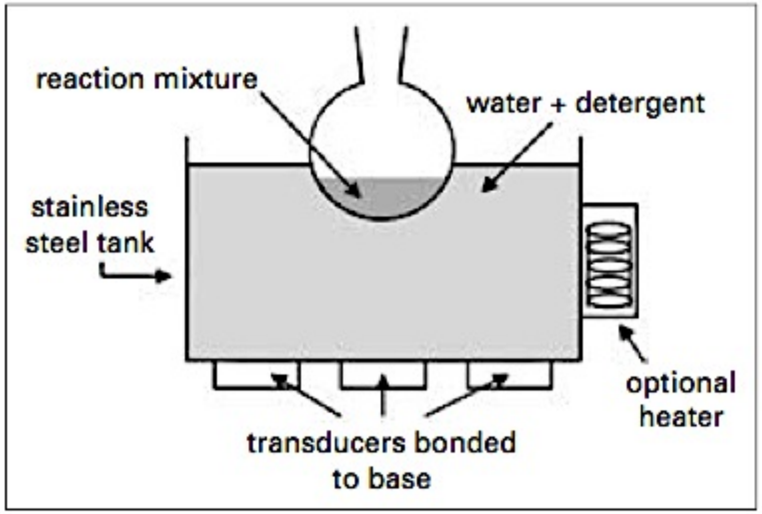


Fig. 16.5 The ultrasonic cleaning bath for sonochemistry.

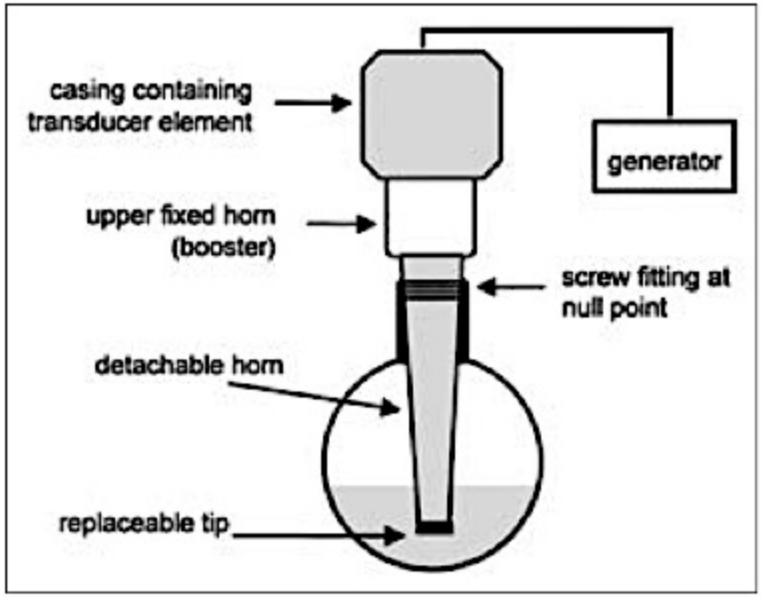


Fig. 16.6 The ultrasonic probe system for sonochemistry.

Equipments

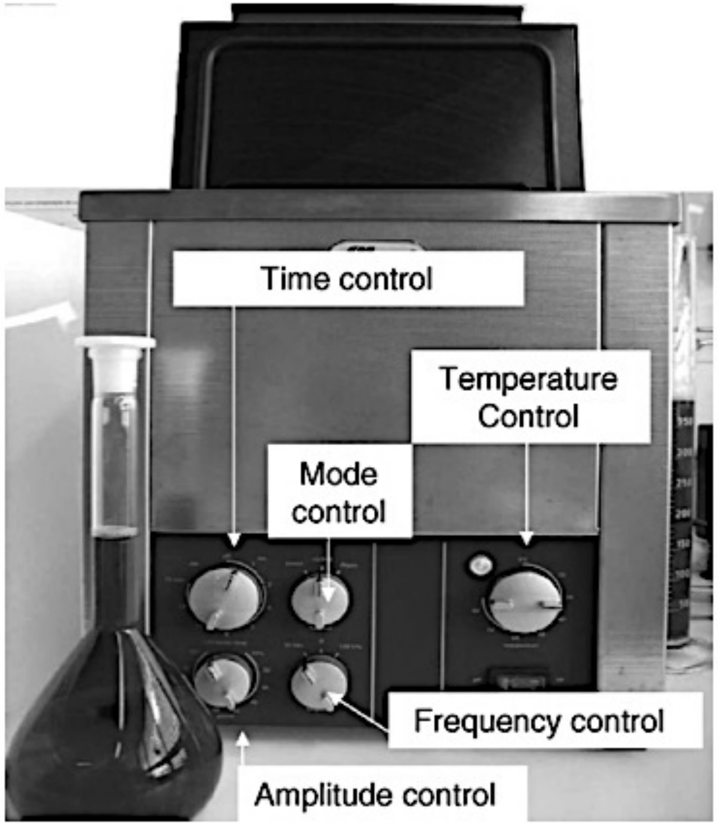


Figure 1.4 A modern ultrasonic bath incorporating the following advances: dual frequency of sonication, variable amplitude of sonication and three different modes of sonication.

1. Dual frequency of sonication.
2. A choice of 25/45 or 35/130 kHz. The baths are designed to work with one of the two frequencies at a time.
3. Power regulation.
4. The intensity of sonication can be controlled through amplitude control (10–100%).
5. Three operation modes:
(a) Sweep: in this mode the frequency varies within a defined range. In this manner the ultrasonic efficiency is more homogeneously distributed in the bath than during standard operation.
(b) Standard
(c) Degas: the power is interrupted for a short period so that the bubbles are not retained by the ultrasonic forces.
6. Heating and timer.

Equipments

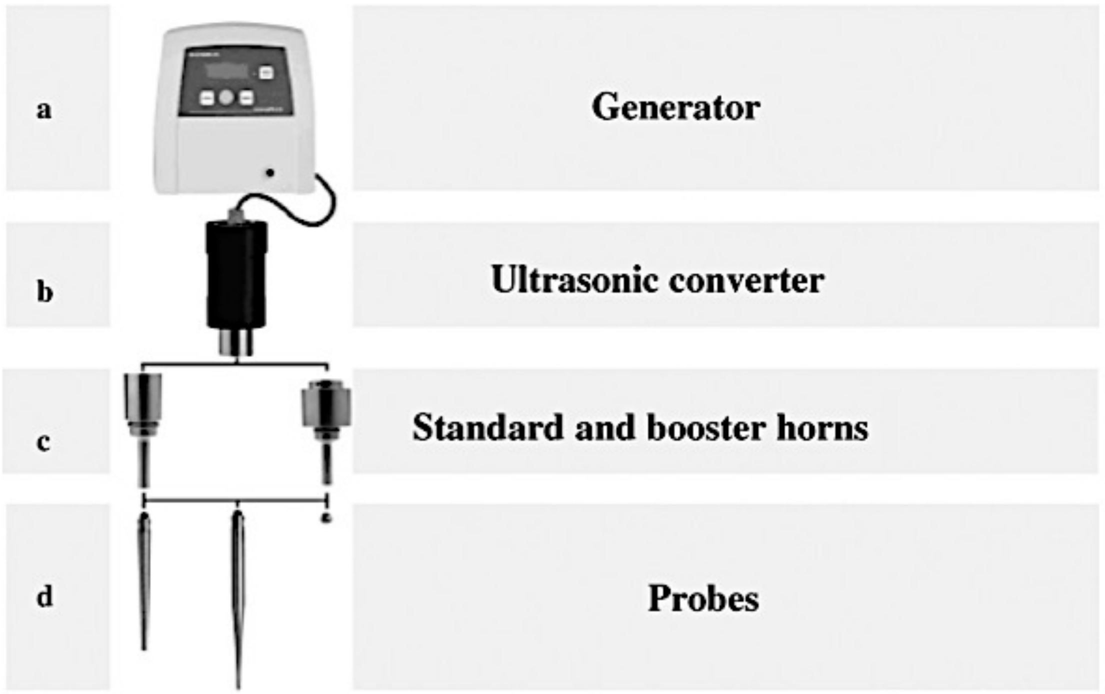


Figure 1.6 An ultrasonic probe. (a) Generator: the generator converts mains voltage into high frequency (20 kHz) electrical energy (most likely, although other frequencies are also available); (b) the converter transforms electrical energy into mechanical vibrations of fixed frequency, normally 20 kHz; (c) standard and booster horns: the horns increase the sonication amplitude; (d) probes: (also called detachable horns) probes transmit ultrasonic energy into the sample. The design is crucial for a good performance. Adapted from the Bandelin company with its kind permission.

Equipments

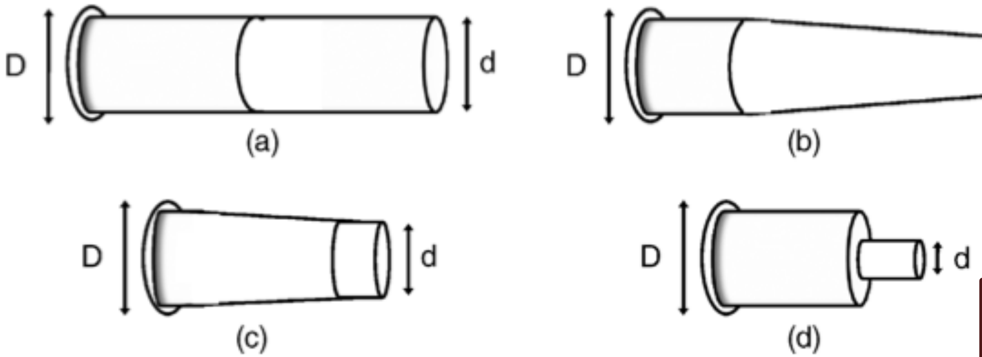


Figure 1.7 Probe shapes: (a) uniform cylinder; (b) exponential taper; (c) linear taper or cone; (d) stepped.

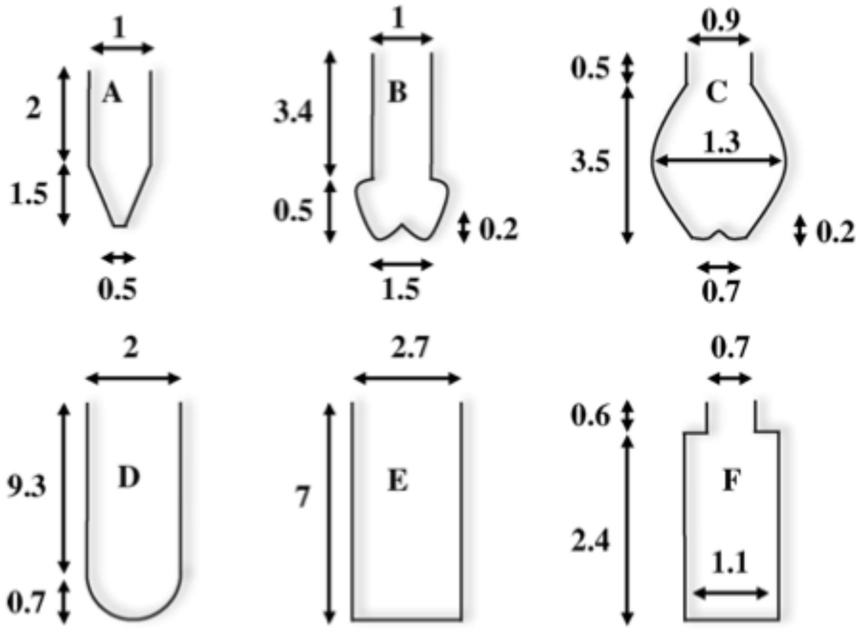


Figure 1.8 The shape of the vessel influences ultrasonic performance. The best forms are those that minimize "dead zones," namely, forms A–C. Adapted from Ref. [13].

Equipments

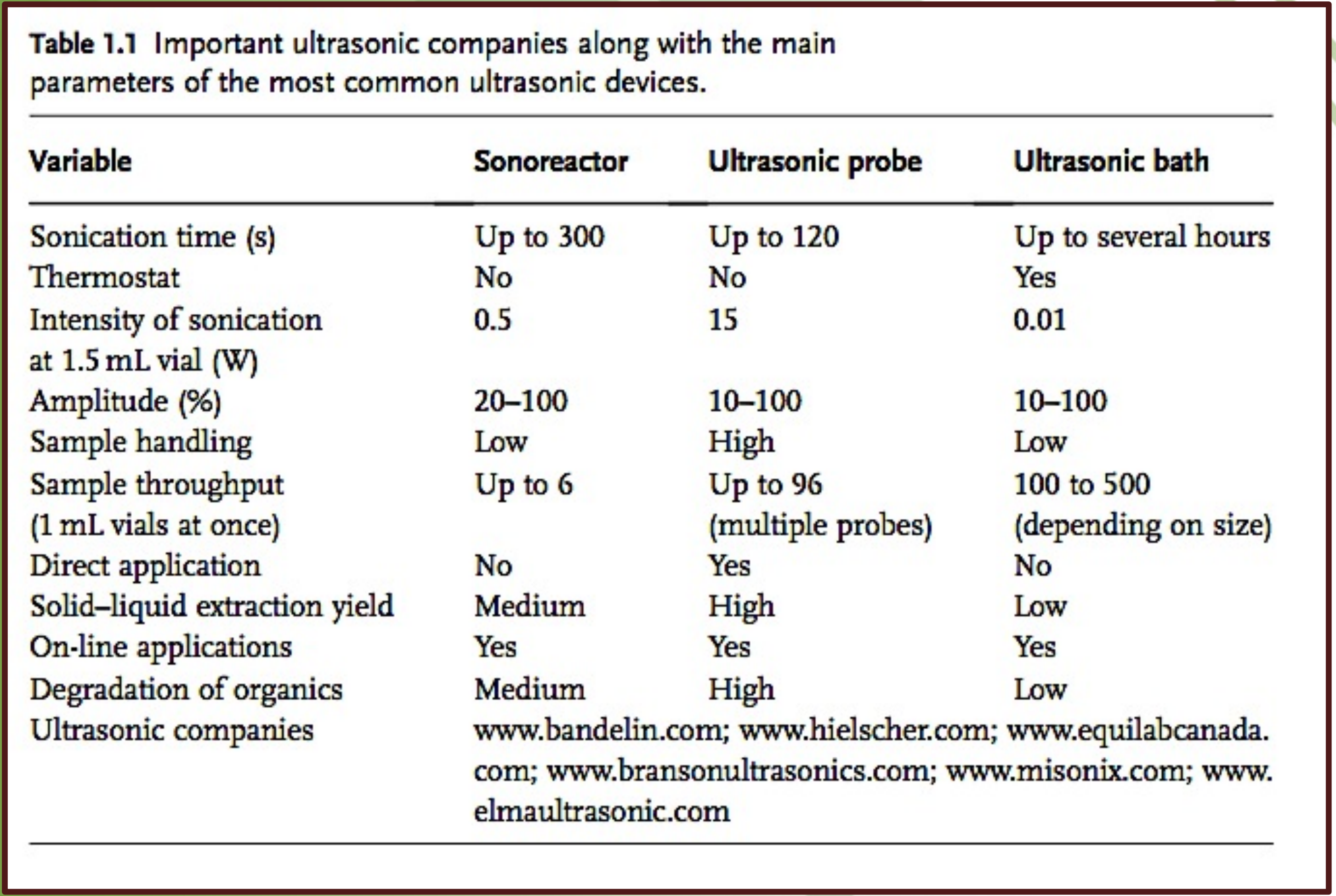
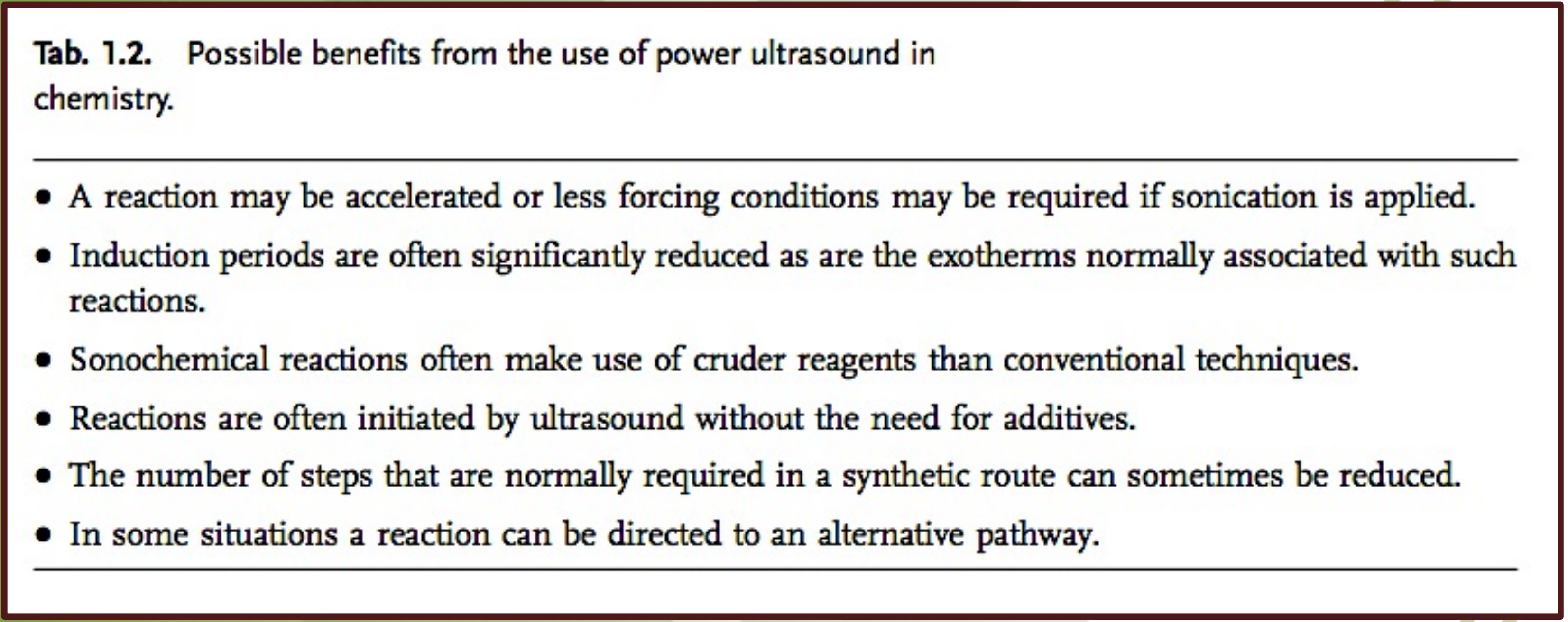


Table 1.1 Important ultrasonic companies along with the main parameters of the most common ultrasonic devices.

Variable	Sonoreactor	Ultrasonic probe	Ultrasonic bath
Sonication time (s)	Up to 300	Up to 120	Up to several hours
Thermostat	No	No	Yes
Intensity of sonication at 1.5 mL vial (W)	0.5	15	0.01
Amplitude (%)	20–100	10–100	10–100
Sample handling	Low	High	Low
Sample throughput (1 mL vials at once)	Up to 6	Up to 96 (multiple probes)	100 to 500 (depending on size)
Direct application	No	Yes	No
Solid–liquid extraction yield	Medium	High	Low
On-line applications	Yes	Yes	Yes
Degradation of organics	Medium	High	Low
Ultrasonic companies	www.bandelin.com; www.hielscher.com; www.equilabcanada.com; www.bransonultrasonics.com; www.misonix.com; www.elmaultrasonic.com		

Sonochemistry



Tab. 1.2. Possible benefits from the use of power ultrasound in chemistry.

- A reaction may be accelerated or less forcing conditions may be required if sonication is applied.
- Induction periods are often significantly reduced as are the exotherms normally associated with such reactions.
- Sonochemical reactions often make use of cruder reagents than conventional techniques.
- Reactions are often initiated by ultrasound without the need for additives.
- The number of steps that are normally required in a synthetic route can sometimes be reduced.
- In some situations a reaction can be directed to an alternative pathway.

Advance in Ultrasonic Technology

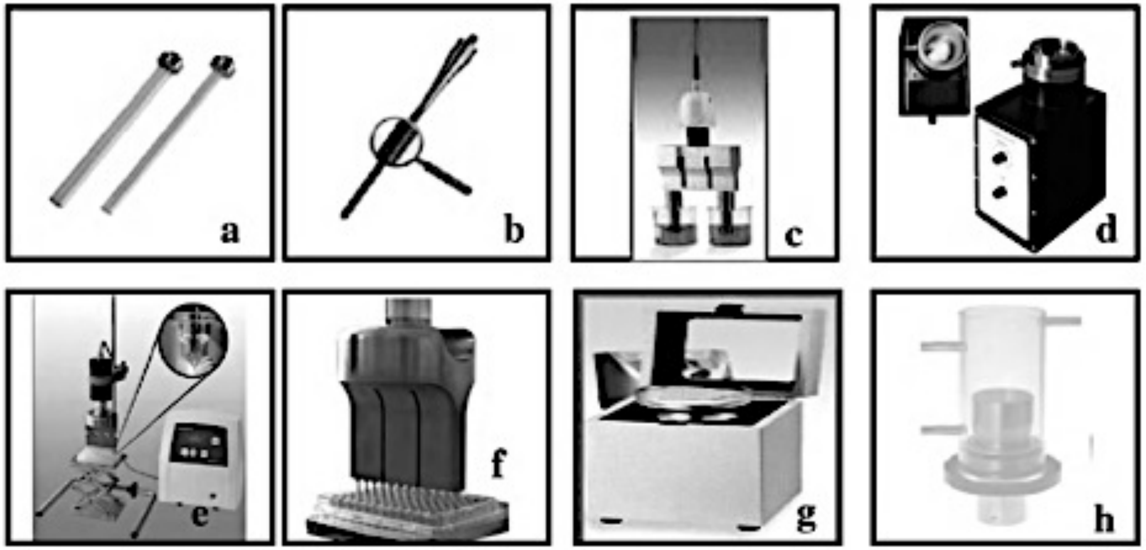
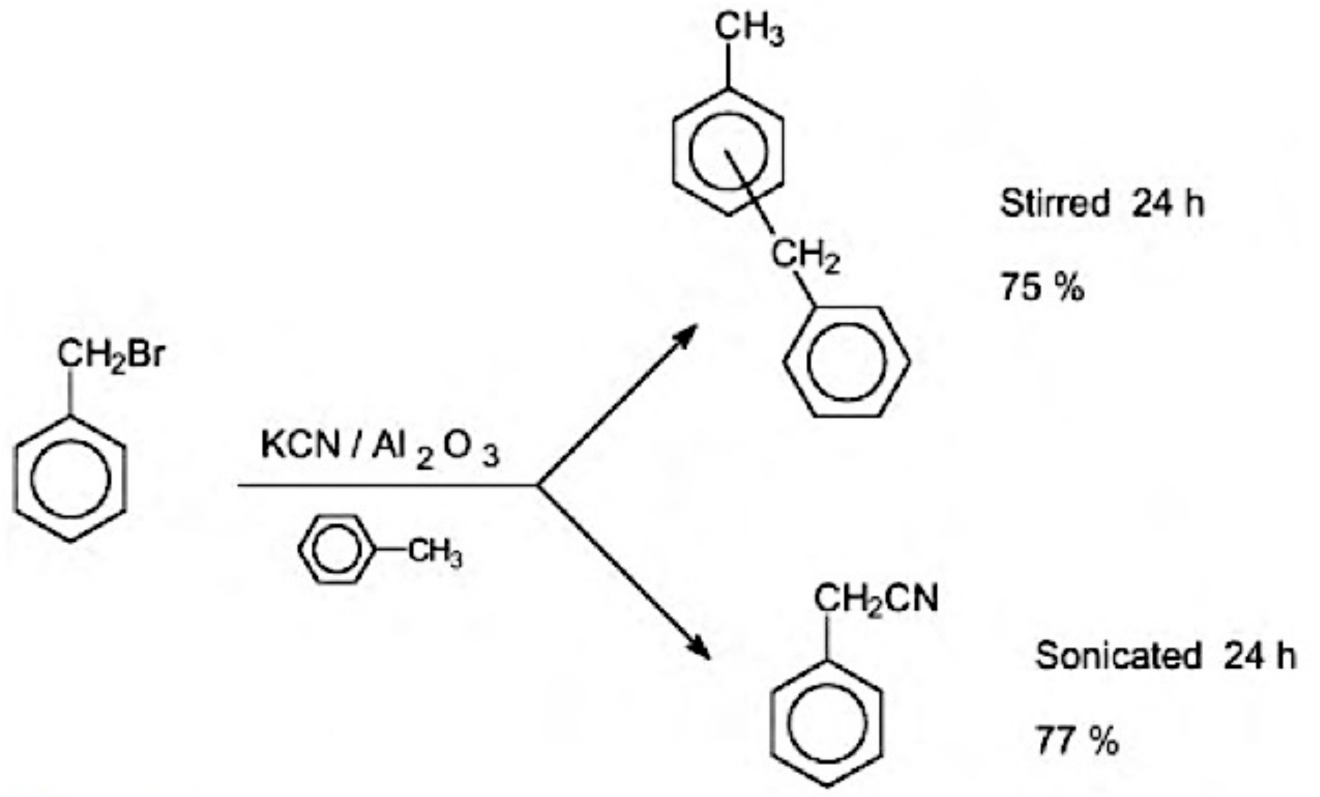


Figure 1.1 Advances in ultrasonic technology: (a) silica glass probe; (b) spiral probe; (c) dual probe; (d) sonoreactor; (e) and (f) multi probe; (g) microplate horns; (h) cup horns. Parts (a,b,e,f and h) are reproduced with permission of the Bandelin company; part (d) is reproduced with permission of the Dr Hielscher company; (c) and (g) are reproduced with permission of Misonix company. Adapted from Ref. [13].

Sonochemistry



Scheme 3.1

Sonochemistry

Rule 1

applies to homogeneous processes and states that those reactions which are sensitive to the sonochemical effect are those which proceed via radical or radical-ion intermediates. This statement means that sonication is able to effect reactions proceeding through radicals and that ionic reactions are not likely to be modified by such irradiation.

Sonochemistry

Rule 2

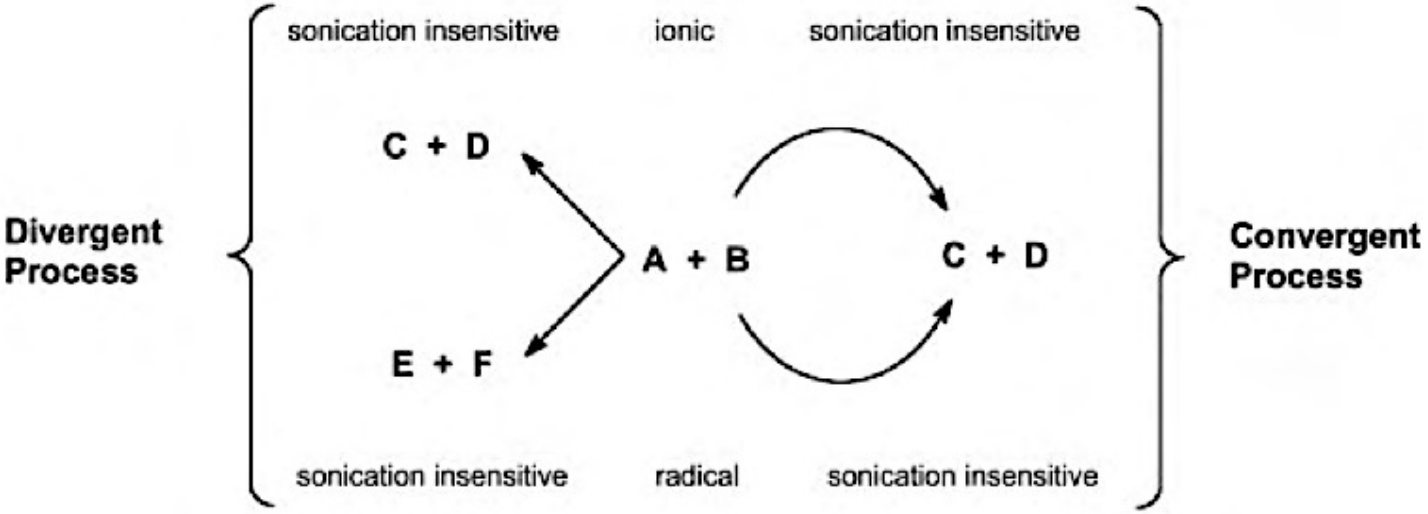
applies to heterogeneous systems where a more complex situation occurs and here reactions proceeding via ionic intermediates can be stimulated by the mechanical effects of cavitational agitation. This has been termed “false sonochemistry” although many industrialists would argue that the term false may not be correct because if the result of ultrasonic irradiation assists a reaction it should still be considered to be assisted by sonication and thus “sonochemical”. In fact the true test for “false sonochemistry” is that similar results should, in principle, be obtained using an efficient mixing system in place of sonication. Such a comparison is not always possible.

Sonochemistry

Rule 3

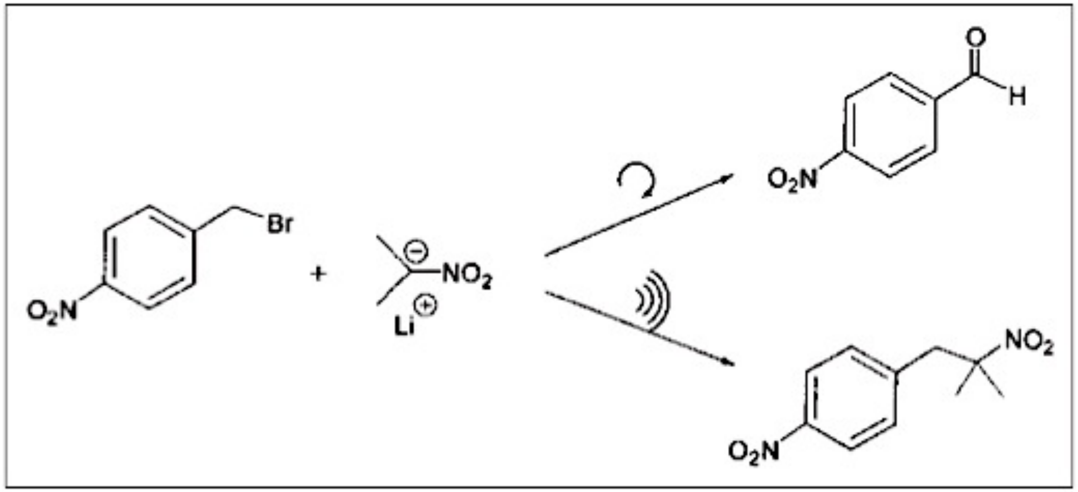
applies to heterogeneous reactions with mixed mechanisms i. e. radical and ionic. These will have their radical component enhanced by sonication although the general mechanical effect from Rule 2 may still apply.

Sonochemistry



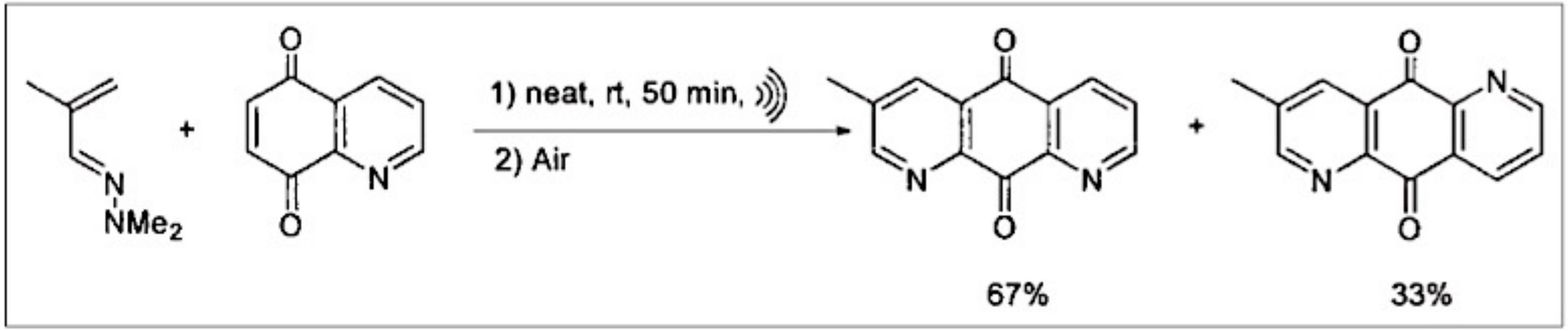
Scheme 3.2

Sonochemistry



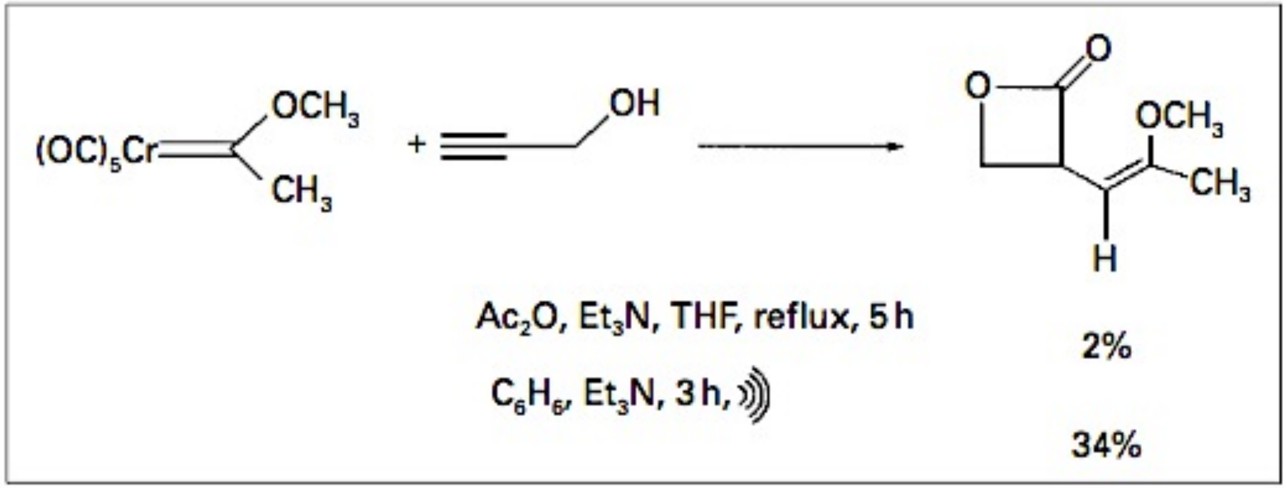
Scheme 16.3 The Kornblum–Russell reaction under mechanical stirring and sonication.

Sonochemistry



Scheme 16.6 Switching of a hetero-Diels–Alder reaction.

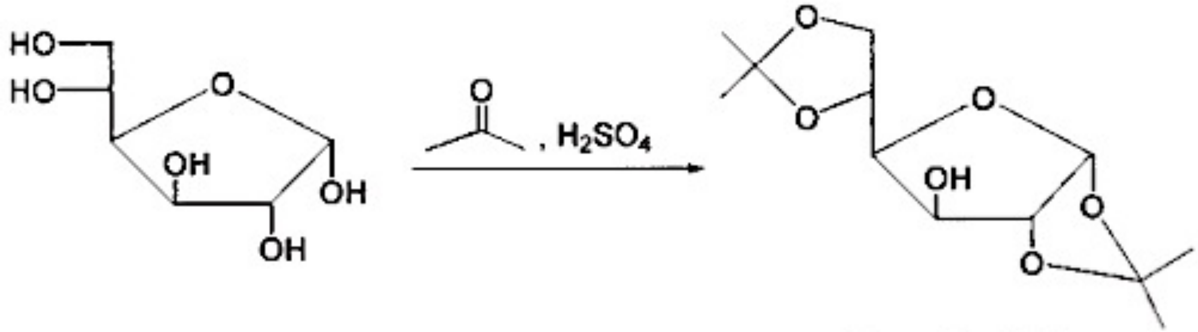
Sonochemistry



Ac_2O, Et_3N, THF, reflux, 5 h — 2%

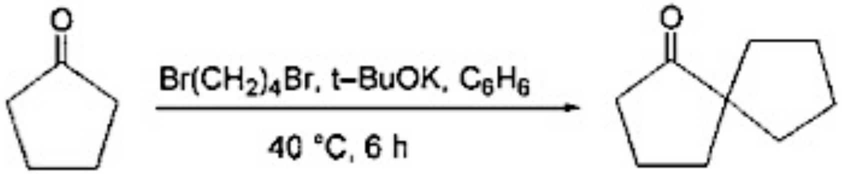
C_6H_6, Et_3N, 3 h,))) — 34%

Sonochemistry



stirring: 5 h, 42%

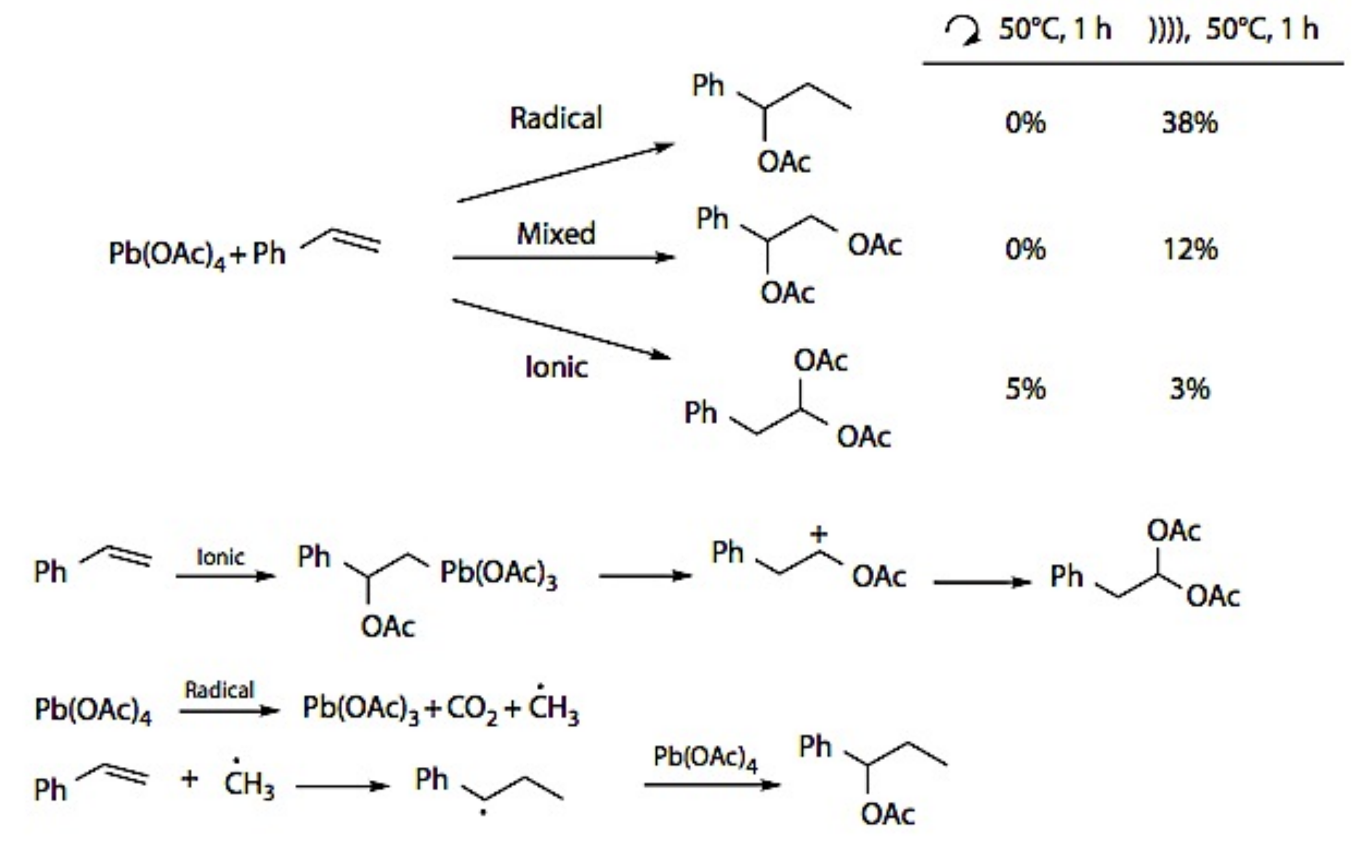
ultrasound: 1 h, 62%



stirring: 14%

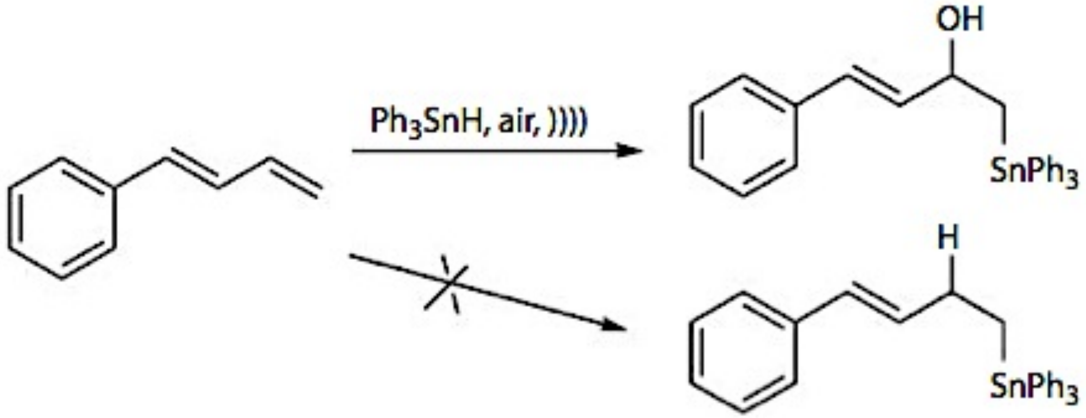
ultrasound: 70%

Sonochemistry



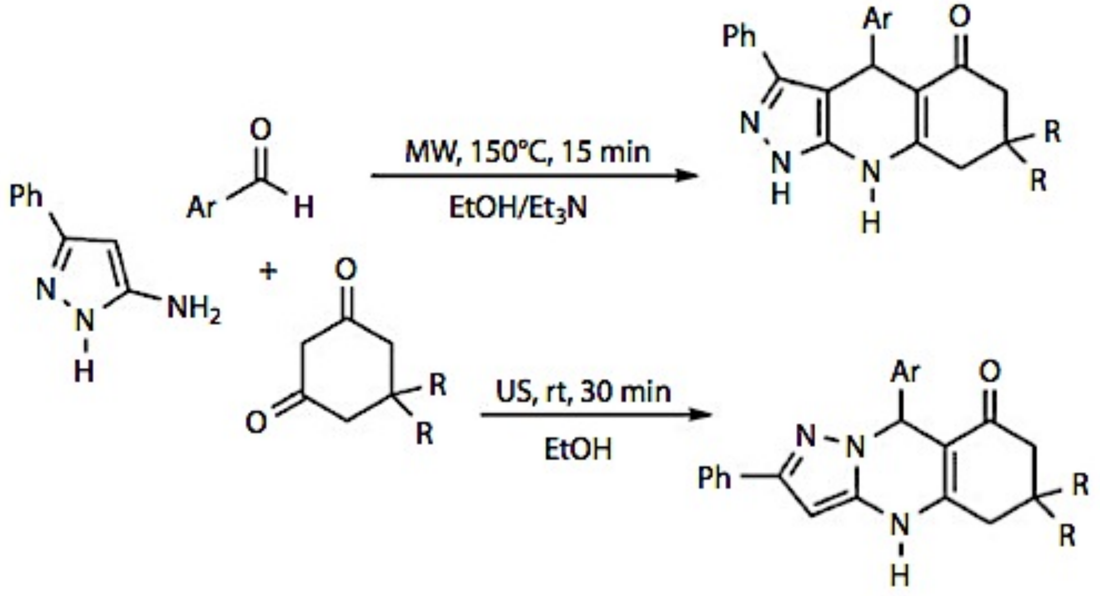
SCHEME 2.5 Divergent pathways observed in the reaction of styrene with $Pb(OAc)_4$.

Sonochemistry



SCHEME 2.6 Hydroxystannation of alkenes under sonochemical activation.

Sonochemistry



SCHEME 2.7 Comparative thermal results for a multicomponent reaction.

Condensation Reactions

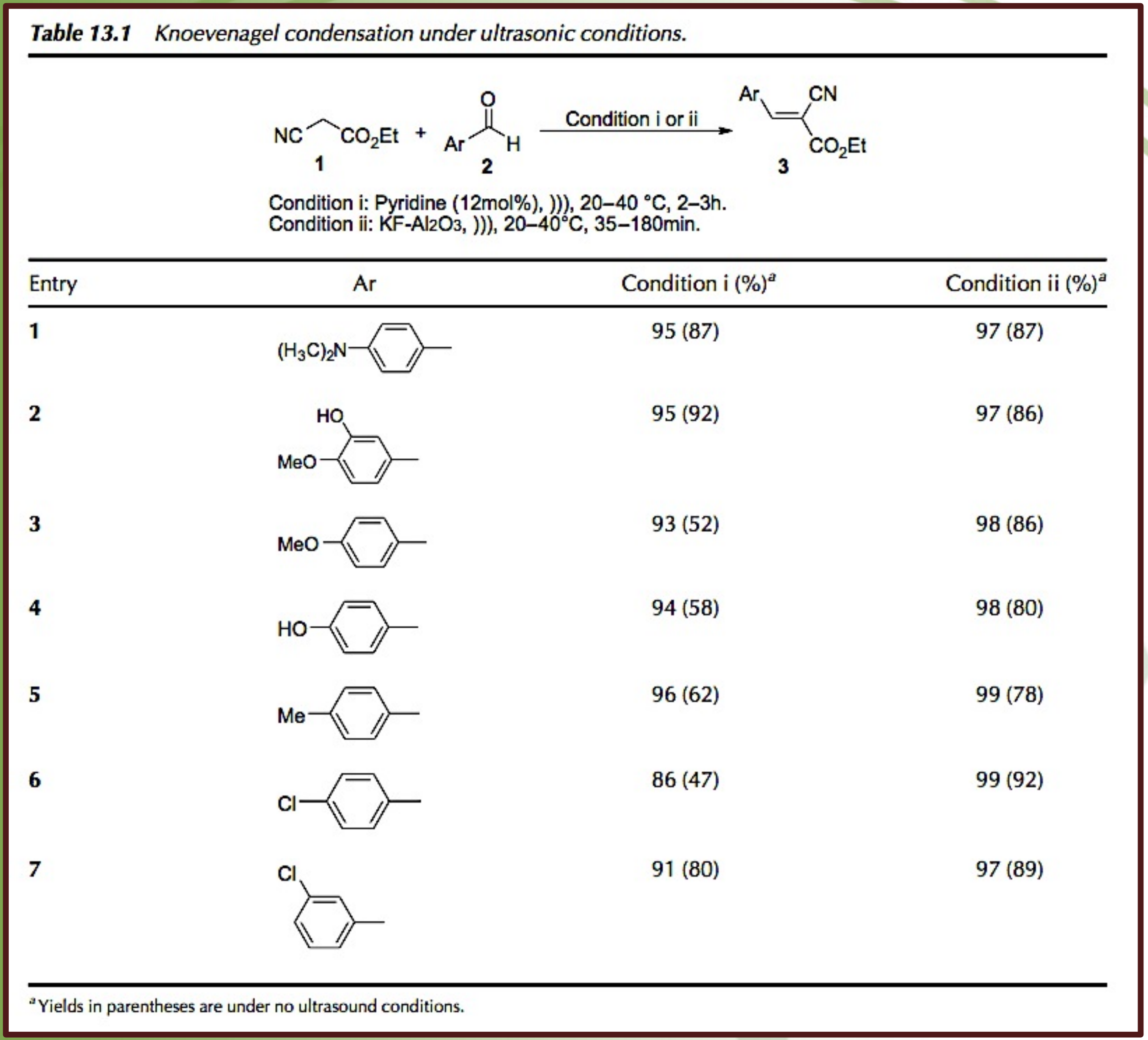


Table 13.1 *Knoevenagel condensation under ultrasonic conditions.*

Condition i: Pyridine (12mol%),))), 20–40 °C, 2–3h.
Condition ii: KF-Al_2O_3,))), 20–40°C, 35–180min.

Entry	Ar	Condition i (%)[a]	Condition ii (%)[a]
1	$(H_3C)_2N$	95 (87)	97 (87)
2	HO MeO	95 (92)	97 (86)
3	MeO	93 (52)	98 (86)
4	HO	94 (58)	98 (80)
5	Me	96 (62)	99 (78)
6	Cl	86 (47)	99 (92)
7	Cl	91 (80)	97 (89)

[a] Yields in parentheses are under no ultrasound conditions.

Condensation Reactions

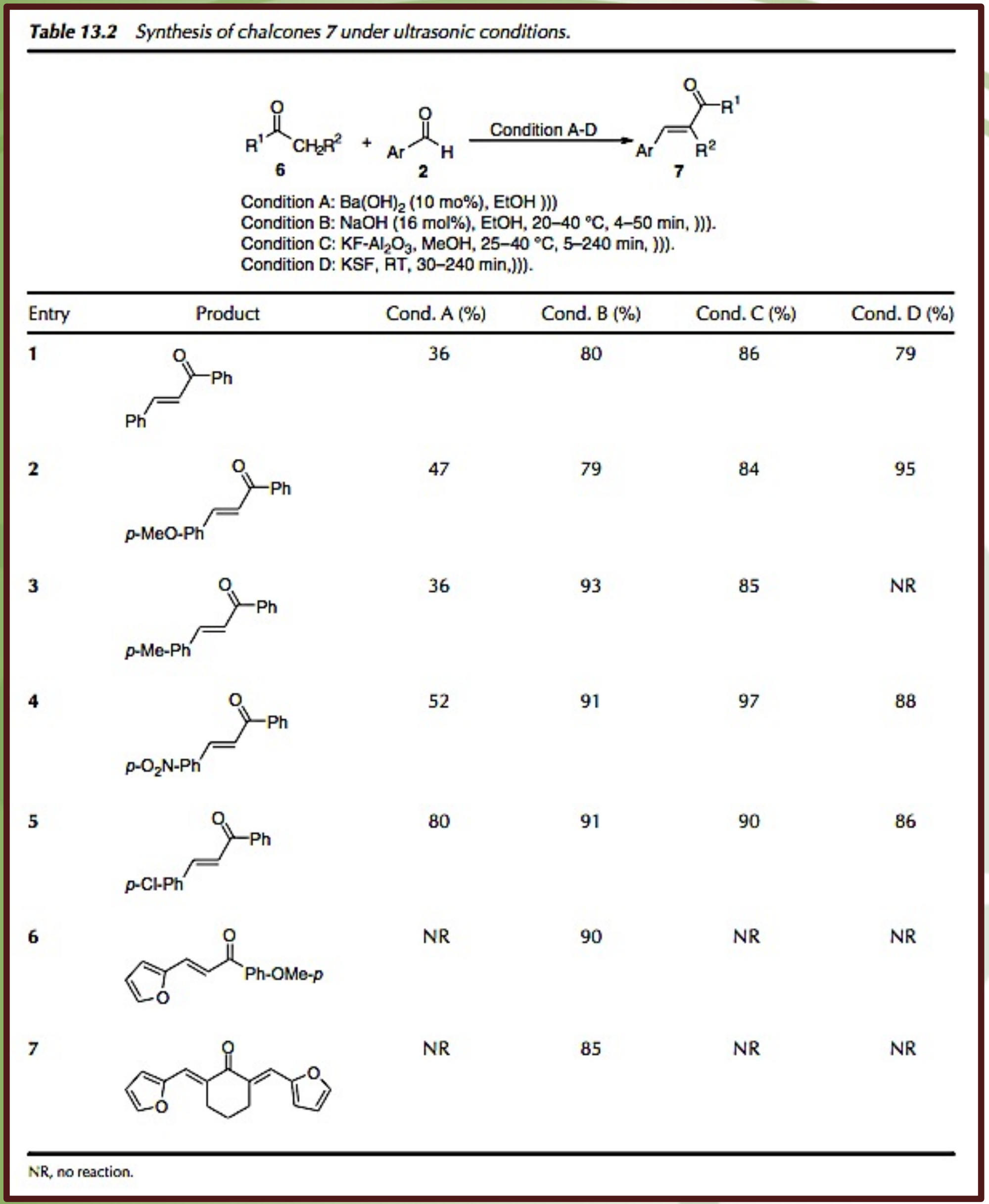


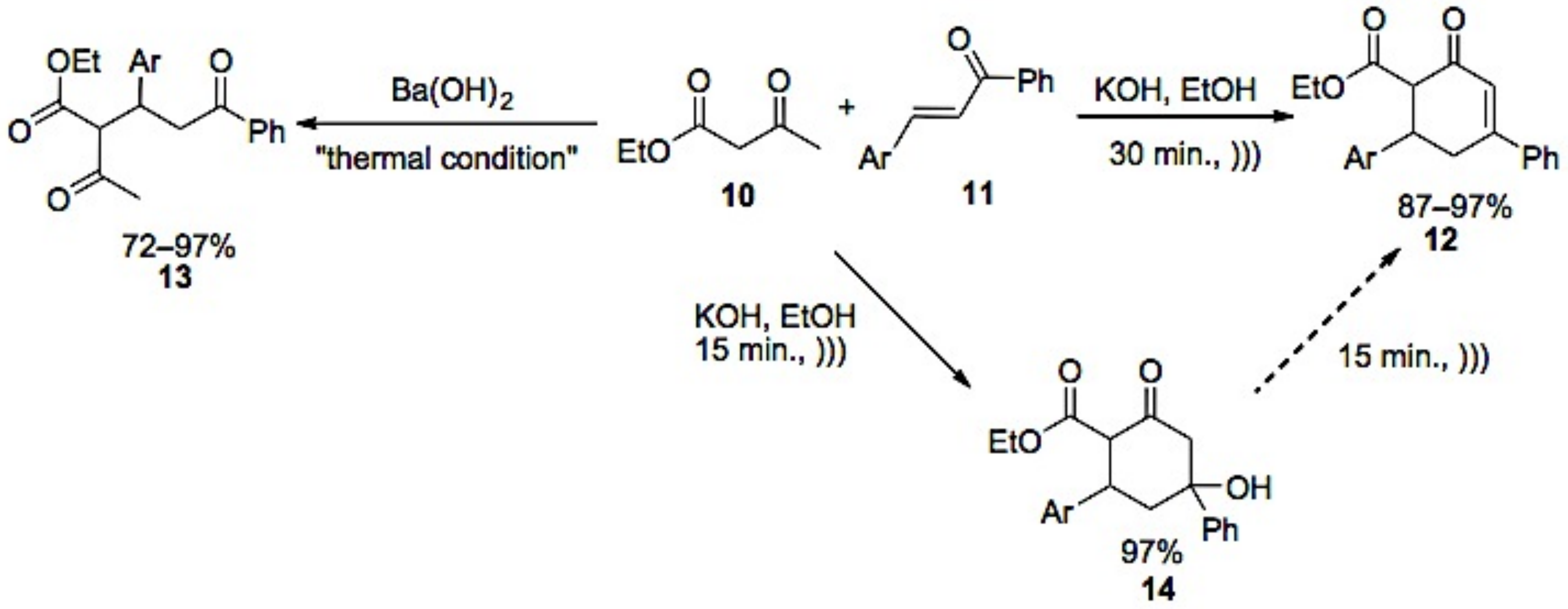
Table 13.2 *Synthesis of chalcones 7 under ultrasonic conditions.*

Condition A: $Ba(OH)_2$ (10 mo%), EtOH)))
Condition B: NaOH (16 mol%), EtOH, 20–40 °C, 4–50 min,))).
Condition C: KF-Al_2O_3, MeOH, 25–40 °C, 5–240 min,))).
Condition D: KSF, RT, 30–240 min,))).

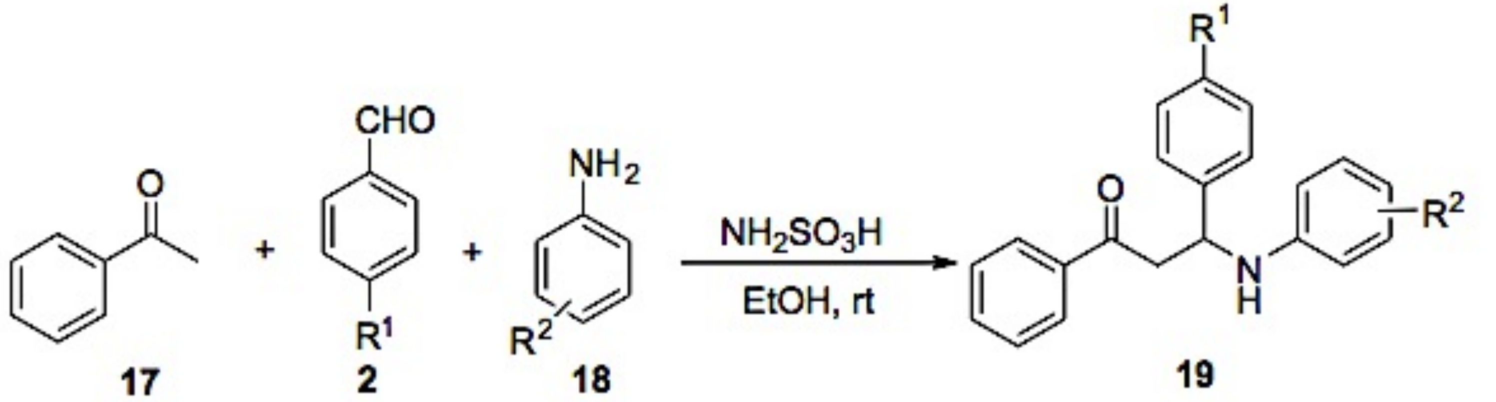
Entry	Product	Cond. A (%)	Cond. B (%)	Cond. C (%)	Cond. D (%)
1	Ph Ph	36	80	86	79
2	Ph p-MeO-Ph	47	79	84	95
3	Ph p-Me-Ph	36	93	85	NR
4	Ph p-O_2N-Ph	52	91	97	88
5	Ph p-Cl-Ph	80	91	90	86
6	Ph-OMe-p	NR	90	NR	NR
7		NR	85	NR	NR

NR, no reaction.

Michael Additions

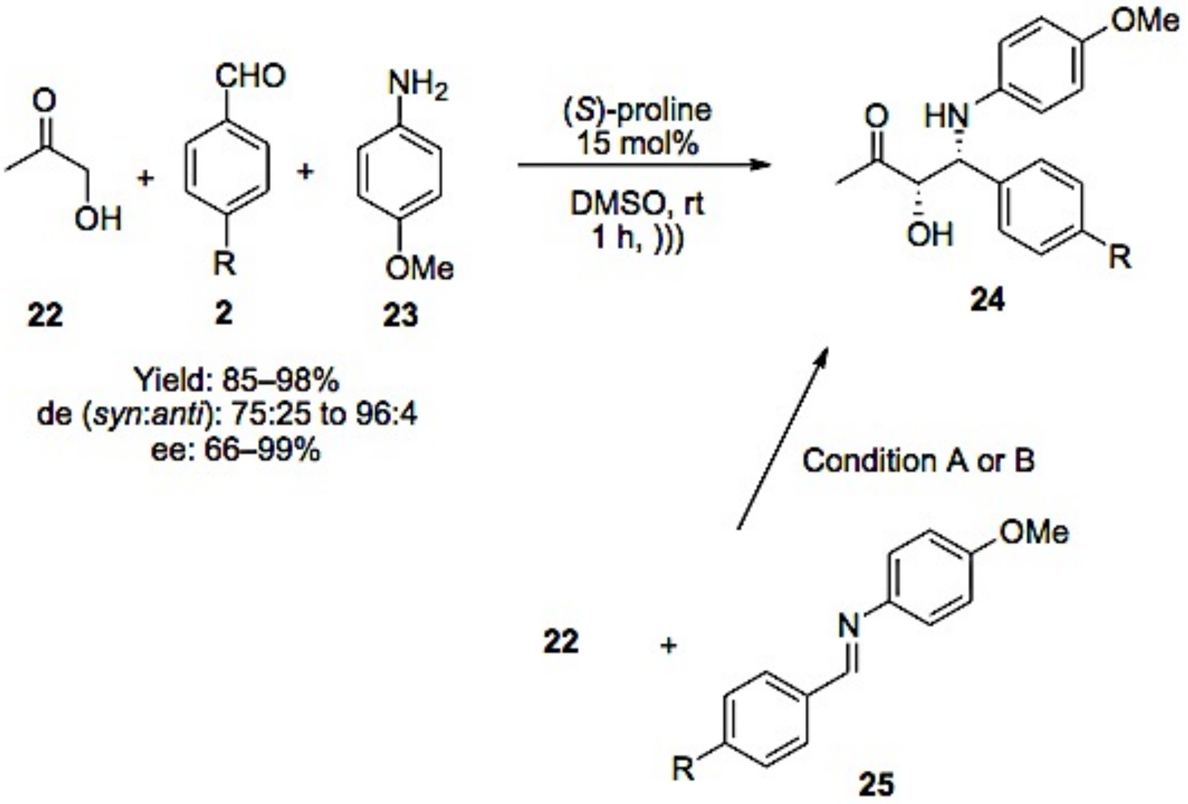


Mannich Reactions



Under US: 2–9 h, 40–97%
Conventional: 18–72 h, 24–90%

Mannich Reactions



Yield: 85–98%
de (*syn*:*anti*): 75:25 to 96:4
ee: 66–99%

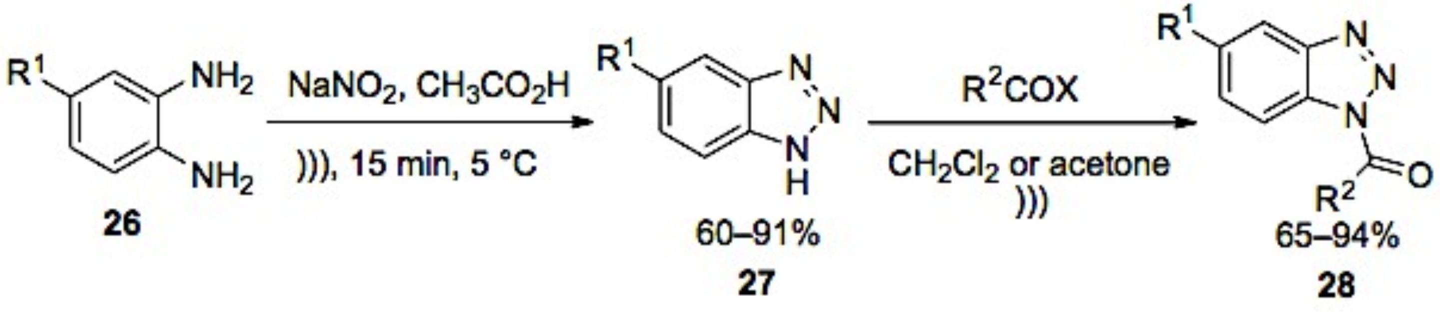
Condition A: (*S*)-proline (15 mol%), DMSO, rt, 1 h,)))

Yield: 90–98%
de (*syn*:*anti*): 75:25 to 96:4
ee: 81–>99%

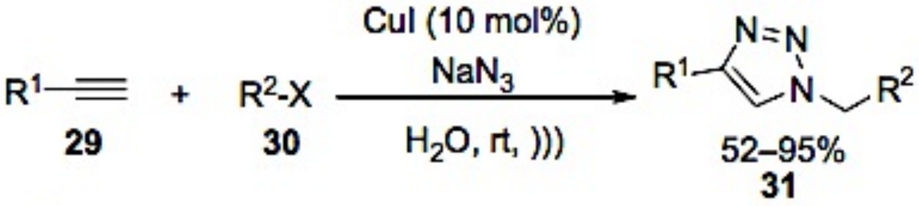
Condition B: (*S*)-proline (15 mol%), DMSO, Δ, 1 h.

Yield: 85–93%
de (*syn*:*anti*): 75:25 to 90:10
ee: 65–93%

Heterocycles Synthesis

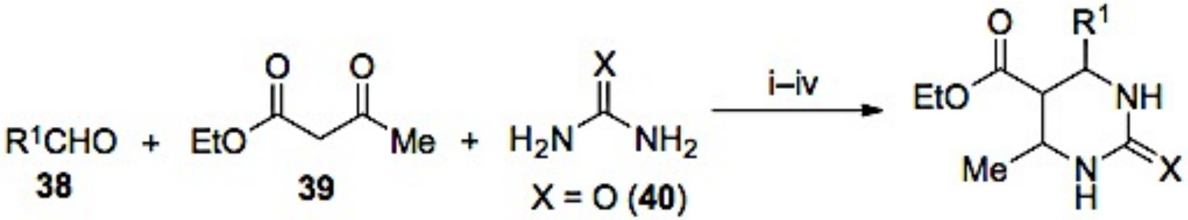


Scheme 13.8



R^1 = Ph, Tol, CH_2OH, $(CH_2)_2OH$
R^2 = Me, Bn, allyl
X = Cl or Br

Heterocycles Synthesis



38

39

X = O (**40**)
X = S (**41**)

42

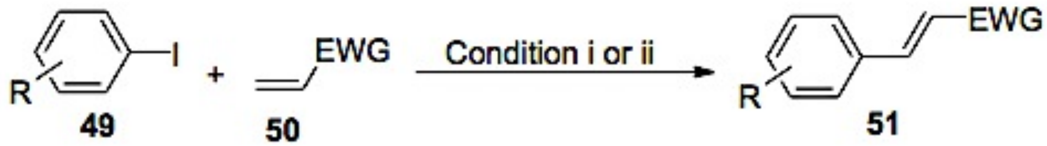
i = EtOH, HCl (drops),))), 2–5 min.
(90–95%)

ii = solvent-free, HCl (1 mol%),))), 15–45 min.
(72–97%)

iii = solvent-free, TFA (5 mol%),))), 45–90 min.
(67–92%)

iv = $[Hbim]BF_4$,))), 40–90 minutes.
(83–97%)

Coupling Reactions

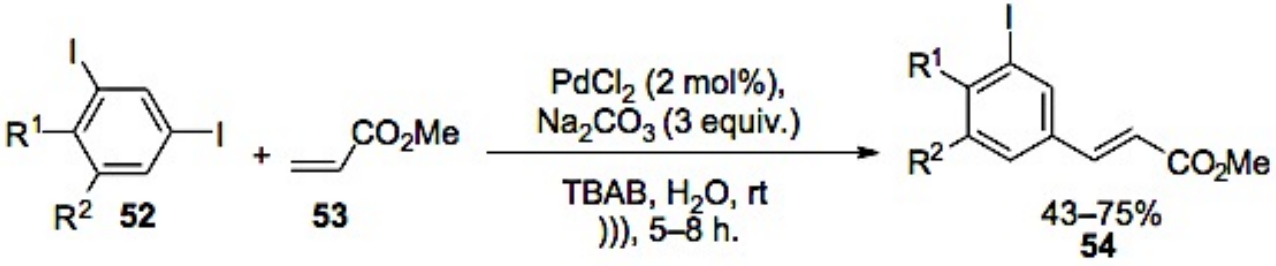


Condition i: Pd(OAc)$_2$ (2 mol%), NaOAc, [bbim]$^+$Br-/[bbim]$^+$BF$_4$-, rt,))) (73–87%).

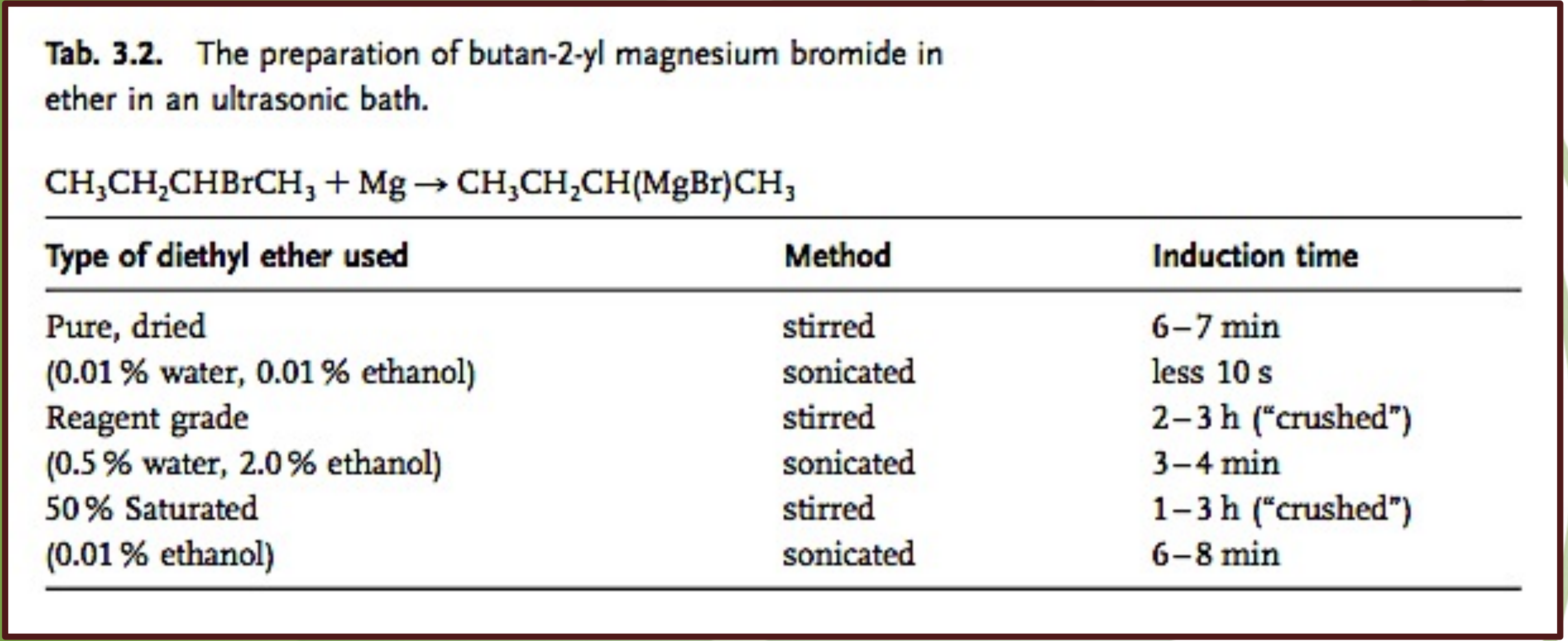
Condition ii: 10% Pd/C, Et$_3$N, NMP, rt,))) (70%).

R = H, MeO, Cl

EWG = H, CO$_2$Me, CO$_2$Et



Sonochemical Activation of Metals



Tab. 3.2. The preparation of butan-2-yl magnesium bromide in ether in an ultrasonic bath.

$CH_3CH_2CHBrCH_3 + Mg \rightarrow CH_3CH_2CH(MgBr)CH_3$

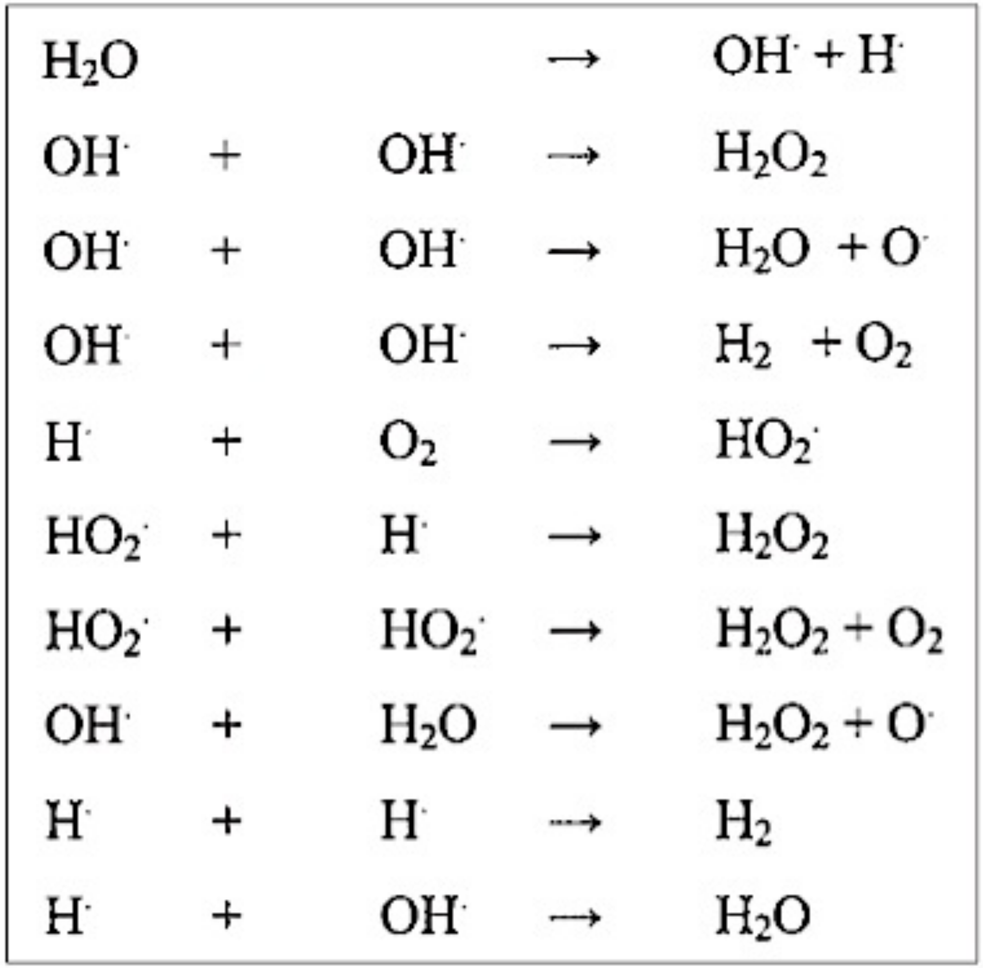
Type of diethyl ether used	Method	Induction time
Pure, dried	stirred	6–7 min
(0.01 % water, 0.01 % ethanol)	sonicated	less 10 s
Reagent grade	stirred	2–3 h ("crushed")
(0.5 % water, 2.0 % ethanol)	sonicated	3–4 min
50 % Saturated	stirred	1–3 h ("crushed")
(0.01 % ethanol)	sonicated	6–8 min

Ultrasound in Environmental Protection

There are three main thrusts to the work on decontamination:

- To use cavitation alone as a clean energy source.
- To use cavitation to improve other treatments (e.g. advanced oxidation).
- To reduce the amounts of chemicals required for conventional treatments (e.g. reduction in biocide levels).

Ultrasound in Environmental Protection



$$H_2O \rightarrow OH^{\cdot} + H^{\cdot}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O + O^{\cdot}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2 + O_2$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

$$HO_2^{\cdot} + H^{\cdot} \rightarrow H_2O_2$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$$

$$OH^{\cdot} + H_2O \rightarrow H_2O_2 + O^{\cdot}$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2$$

$$H^{\cdot} + OH^{\cdot} \rightarrow H_2O$$

Scheme 16.18 Sonochemical decomposition of water.