ULTRASOUND IN SYNTHESIS

Kenneth S. Suslick

School of Chemical Sciences
University of Illinois at Urbana-Champaign
505 S. Mathews Av.
Urbana, Illinois 61801
U.S.A.

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1. INTRODUCTION AND INTENT

The chemical[1] and biological[2] effects of ultrasound were first reported by Loomis more than 50 years ago. In spite of early work in the area of sonochemistry, interest within the chemical community remained exceedingly modest until the past few years. With the advent of inexpensive and reliable sources of ultrasound, however, increasing use of sonochemistry in a variety of reactions is being reported. The purpose of this review is to act as a critical introduction for those interested in the chemical effects of ultrasound and the synthetic applications of sonochemistry. In addition, a brief overview of the physics of acoustic cavitation is presented in order to explain the origin of sonochemical reactivity. Interested readers are referred to earlier reviews of general sonochemical phenomena.[3,4,5]

Some of the terminology in this area will be unfamiliar to most chemists. Cavitation is the formation of gas bubbles (or cavities) in a liquid and occurs when the pressure within the liquid drops sufficiently lower than the vapor pressure of the liquid. Cavitation can occur from a variety of causes: turbulent flow, laser heating, electrical discharge, boiling, radiolysis, or acoustic irradiation. We will be concerned exclusively with acoustic cavitation. When sound passes through a liquid, it consists of expansion (negative-pressure) waves and compression (positive-pressure) waves. These cause vapor and gas-filled bubbles to grow and recompress. Acoustic cavitation can lead, as discussed later, to an implosive collapse of such cavities with associated high-energy chemistry. The importance of acoustic cavitation extends well beyond its chemical effects, and is relevant to studies of heat transport, liquid tensile strengths, and superheating and boiling phenomena.[6,7] Furthermore, since ultrasound is heavily used both for medical treatment (hyperthermia for soft tissue traumas) and diagnosis (sonography of fetal development), the biological and chemical effects of ultrasound are of immediate importance to the health services community.[8,9,10] We will use the symbol, -)-)-)→ , in this review to indicate ultrasonic irradiation or "sonication" of a solution leading to a sonochemical reaction. Sonocatalysis will be restricted in its use only to the creation of a catalytically competent intermediate by ultrasonic irradiation; we will not refer to a simple sonochemical rate enhancement of an already ongoing reaction by this term.

2. ORIGINS OF THE CHEMICAL EFFECTS OF ULTRASOUND

The velocity of sound in water is ≈1500 m/sec; ultrasound spans the frequencies of 20 KHz to 10 MHz, with associated acoustic wavelengths of 7.6 to 0.015 cm. Clearly no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry. Instead, the chemical effects of ultrasound derive from several different physical mechanisms, depending on the nature of the system. All represent "non-linear" acoustic phenomena: the propagation of high amplitude sound waves results in effects which can be described only with the inclusion of terms not linear with the acoustic wave's displacement amplitude. An extensive literature dealing with nonlinear propagation of sound exists[7,11,12], but is beyond the scope of this review.

Acoustic cavitation can be considered to involve at least three discrete stages: nucleation, bubble growth, and, under proper conditions, implosive collapse. The dynamics of cavity growth and collapse are strikingly dependent on local environment, and one must therefore consider separately cavitation in a homogeneous liquid and cavitation near a liquid-solid interface.

2.1. The Nature of Acoustic Cavitation

The tensile strength of a pure liquid is determined by the attractive intermolecular forces which maintain its liquid state. On that basis the calculated tensile strength of water, for example, is in excess of -1000 atmospheres.[13] In practice however, the measured threshold for initiation of cavitation is never more than a small fraction of that: tap water will cavitate at a negative acoustic pressure of a few atmospheres. The tensile strength increases upon purification, but even after exhaustive purification and submicron filtering, water will withstand only -200 atmospheres for a few seconds.[14] One also needs to rationalize two other methods which increase the cavitation threshold: vacuum degassing[15], and initial hydrostatic pressurization[16]. Indeed, if the observed tensile strengths of liquids did approach their theoretical limits, the acoustic intensities required to initiate cavitation would be well beyond that generally available, and no sonochemistry would be observed in homogeneous media!

These observations demonstrate that cavitation is initiated at a nucleation site where the tensile strength is dramatically lowered. An obvious site would be small gas bubbles present in the liquid. Free gas bubbles, however, are caught in a double bind: small ones of the size needed for acoustic cavitation (a few microns in radius) will redissolve in a few seconds, whereas larger one will rapidly rise to the surface.[17] The nucleation mechanism generally accepted at this time involves gas entrapped in small-angle crevices of particulate contaminants,[18,19,20] as shown schematically in Figure 1. As the crevice-stabilized nucleus is subjected to large, negative acoustic pressures, the bubble volume grows, releasing small free bubbles into solution or undergoing violent collapse itself. Those actions which remove such nucleation sites (e.g., ultrafiltration to remove particulates, evacuation or pressurization to flood the crevices, etc.) will thus increase the cavitation threshold. In liquids undergoing cavitation, one should note that after the initial cycle of cavitation, the implosive collapse of bubbles generates microcavities which can then serve as nucleation sites for the next cycle.[21]

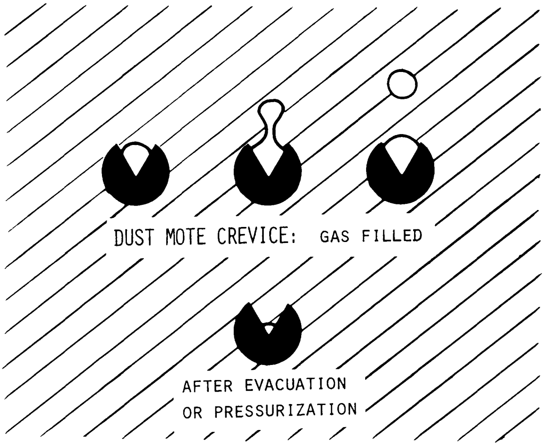


Figure 1. Nucleation of Acoustic Cavitation.

2.2. Cavitation in Homogeneous Media

Flynn proposed the generally accepted division of cavitation phenomena in homogeneous liquids into 1) transient cavitation, in which a short-lived bubble undergoes large excursions of size in a few acoustic cycles and may terminate in a violent collapse, and 2) stable cavitation, in which a bubble oscillates many times with limited change about its equilibrium radius.[22] Both stable and transient cavitation may occur simultaneously in a solution, and a bubble undergoing stable cavitation may change to transient cavitation if the radius becomes suitable for efficient collapse. It is primarily transient cavitation which gives rise to sonochemistry. An idealized pictorial representation of this scheme is shown in Figure 2. Several exhaustive reviews of acoustic cavitation dynamics have been published,[6,23,24,25] so this discussion will be limited to a qualitative overview.

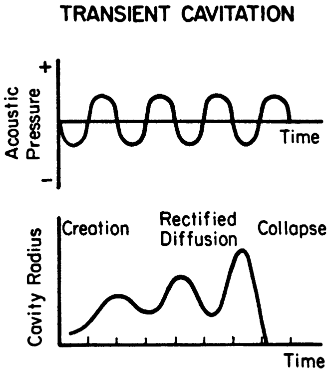


Figure 2. Idealized Representation of Bubble Growth and Collapse During Transient Cavitation.

The oscillatory behavior of cavities in an acoustic field has been well-described by a variety of mathematical models derived from Rayleigh's original approach with the inclusion of various non-ideal liquid properties.[26,27,28,29,30,31] One can easily calculate from such equations the resonant size of a cavity under ultrasonic irradiation (i.e. that size bubble which will undergo maximum expansion). Minnaert first derived[32] this resonant size from a simplified model which assumed a non-condensable gas and neglected viscosity. More complete determinations[6] do not lead to significant corrections for frequencies less than 300 KHz. At 20 KHz, a typical frequency of laboratory ultrasonic irradiations, this resonant radius is calculated to be 170 μm, and at 1 MHz, 3.3 μm.

Bubbles which are well below this optimal size will still undergo transient cavitation if the acoustic field is sufficiently large. Given a well-defined acoustic field, one would wish to know which size cavities will undergo transient cavitation, which will undergo stable cavitation, and which will simply redissolve. One may calculate a threshold for transient cavitation (the "Blake" threshold), in which the bubble grows rapidly under the instigation of the expansion wave of a single acoustic cycle.[33,34,35,36] Bubbles much larger than this will not be capable of undergoing transient cavitation due to a non-negligible inertial term: they would be unable to respond to the imposed pressure changes within the time frame of the acoustic frequency.

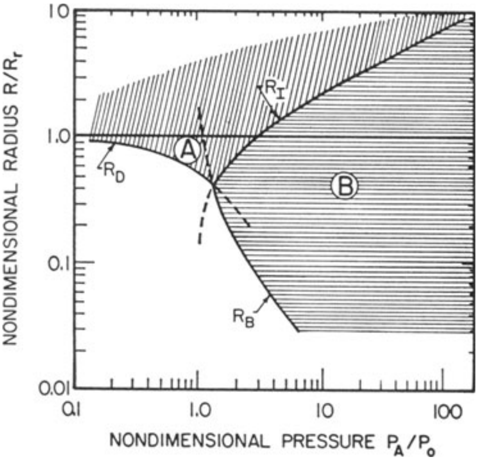


Figure 3. **Thresholds of Cavitation.** [After R. E. Apfel[6]]

Region A: Bubble growth through rectified diffusion only.

Region B: Bubble growth through transient cavitation.

R_D: Threshold for rectified diffusion.

R_I: Threshold for predomination of inertial effects.

R_B: Blake threshold for transient cavitation.

Cavities below this resonant size are also capable of slow growth over a number of acoustic cycles through the process known as rectified diffusion.[37,38] Even when far from resonance with the sound field, a bubble will undergo small oscillations. Since the surface area of such a bubble is slightly larger during the negative pressure portion of an acoustic cycle than during the positive pressure portion, more gas will diffuse into the bubble during expansion than will diffuse out again during recompression. Thus, gas will be acoustically pumped into the bubble. The effect is very small per cycle, but is cumulative and becomes significant over many cycles, leading to bubble growth up to the Blake threshold. Very small bubbles will not grow during ultrasonic irradiation as fast as they redissolve, and therefore will not lead to cavitation. These results can be graphically represented in Figure 3, where the various domains of bubble dynamics are represented in terms of bubble radius and acoustic pressure.

The dynamic process of bubble collapse has been observed by Lauterborn and others by ultrahigh speed photography (10^5 frames/sec) of laser generated cavitation.[39] As seen in Figure 4, the comparison between theory and experiment is remarkably good. These results were obtained in silicone oil, whose high viscosity is responsible for the spherical rebound of the collapsed cavities. The agreement between theoretical predictions and the experimental observations of bubble radius as a function of time are particularly striking.

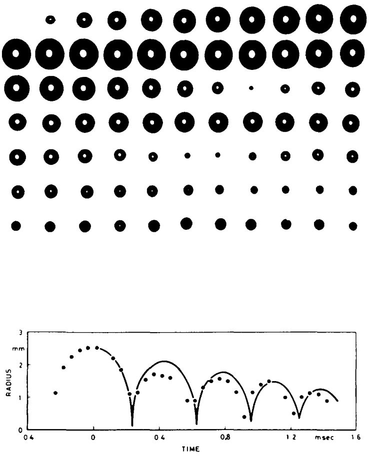


Figure 4. Dynamics of Bubble Motion: Laser-induced cavitation in silicone oil. Upper: experimental observations at 75,000 frames/sec; Lower: experimentally observed radius vs. theory. [W. Lauterborn[39]]

Given this detailed understanding of the dynamics of cavitation, the relevant question for the chemist lies in the actual mechanisms responsible for sonochemical reactions in homogeneous media. Historically, there have been two separate proposals: "hot-spot" pyrolysis[40,41] and electrical discharge[42,43]. The implosive collapse of a bubble will produce adiabatic heating of its contents: estimates of the conditions so induced are in the thousands of degrees and thousands of atmospheres, as discussed shortly. The several proposals of electrical discharge during cavitation (including more recent suggestions[44,45]) have not been well-developed on a molecular level and recently have been thoroughly rebutted as inconsistent with observed sonochemical reactivities and sonoluminescent behavior.[46,47] Two other, more limited mechanisms for homogeneous sonochemistry have been suggested. The cleavage of very large polymers involves direct mechanical cleavage either by shock waves generated during transient cavitation or by the intense accelerations caused by the sound field itself ($\approx 10^5$ g at 500 KHz).[48] Secondary reactions with high energy species produced from solvent sonolysis also contributes to polymer degradation. Finally, generally small rate enhancements of solvolysis reactions have been reported[49,50,51] (<20%, although there is one report of an tenfold increase[52]), and interpreted in terms of a disruption of the solvent structure[53] by the ultrasonic irradiation. The details of this proposed mechanism remain undiscussed.

The high temperatures and pressures created during transient cavitation are difficult both to calculate and to determine experimentally. The simplest models of cavitation were proposed in 1917 by Lord Rayleigh, who first described[54] the collapse of cavities in incompressible liquids and predicted enormous local temperatures (10,000 K) and pressures (10,000 atm) during such collapse; these calculations, however, neglect heat transport and the effects of condensable vapor. More realistic estimates from increasingly sophisticated hydrodynamic models yield estimates of ≈5000 K and ≈1000 atmospheres with effective residence times of <100 nsec, but are very sensitive to initial assumptions of the boundary conditions.[28,29,30]

Experimental determinations of cavitational conditions are extremely limited. The first involved spectral analysis of sonoluminescent emission[55] of excited state alkali metal atoms generated upon sonolysis of aqueous salt solutions. The results of these studies give estimates of effective temperatures in the range of 3400 K; the assumption is made, however, that the site of luminescence is within the cavitation event. Since sodium ions are involatile, the observed luminescence must be due to species formed outside of the original cavitation zone by secondary reactions, perhaps in a heated liquid shell surrounding the cavity.[56] The second probe of cavitation conditions, which also relied on sonoluminescence data, utilized the relative emissivity of NO and NO_2 saturated water and estimated temperatures of ≈1000 K in aqueous solutions irradiated at 459 KHz.[57] The most recent experimental determination of cavitational temperature directly deals with the conditions which give rise to sonochemistry by utilizing the comparative-rate, "chemical thermometry" approach, originally used[58] in shock tube experiments. In this work, the relative rates of CO dissociation of metal carbonyls were determined as a function of metal carbonyl vapor pressure[59,60] and then analyzed using activation parameters previously determined by gas-phase laser pyrolysis. Both a gas-phase and a liquid-phase reaction zone were observed and the latter interpreted in terms of a heated liquid shell as shown in Figure 5; the liquid zone was estimated to extend about 200 nm from the surface of the bubble, and to have a lifetime of less than 2 μsec. The effective temperatures were determined to be 5200 K for the gas-phase site and ≈1900 K for the liquid shell, in alkane solvents sonicated under Ar at 20 KHz with an overall vapor system pressure of 5.0 torr.

Given the differences in irradiation conditions (frequencies, solvents, system vapor pressures, etc.) used in these various studies, it is not yet possible to determine the extent of real differences among these estimates. Regardless of the details, however, it is clear that cavitational collapse is producing hot-spots with effective temperatures of several thousand degrees. In addition, the importance of substrate volatility should be emphasized, since the predominant site of most sonochemistry is the gas-phase reaction zone, rather than the surrounding heated shell.

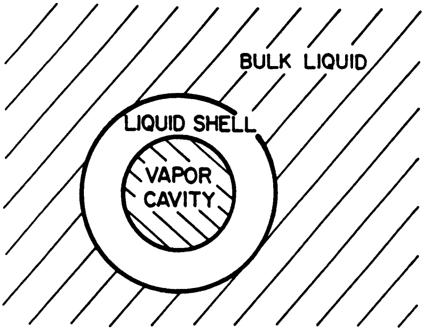


Figure 5. The Two Site Model of Sonochemical Reaction Zones.

2.3. Cavitation at Surfaces

The principal effect of ultrasound on liquid-liquid interfaces between immiscible fluids is emulsification. This is one of the major industrial uses of ultrasound,[61,62,63] and a variety of apparatus have been devised which will generate micron-sized emulsions.[7] The mechanism of ultrasonic emulsification lies in the shearing stresses and deformations of larger droplets induced by the sound field. When these stresses become greater than the interfacial surface tension, the droplet will burst.[64,65] The chemical effects of emulsification lie principally in the greatly increased surface area of contact between the two immiscible liquids. Results not unlike phase transfer catalysis may be expected.

Acoustic streaming is another non-linear acoustic phenomenon important to the effect of ultrasound on surfaces.[7,66] This time-dependent flow of liquid induced by a high intensity sound field is independent of cavitation. Its origins lie in the conservation of momentum. As a liquid absorbs energy from a propagating acoustic wave, it must also acquire a corresponding momentum, thus creating force gradients and mass transport. Therefore, when a liquid-liquid or liquid-solid interface is exposed to ultrasound, improved mass transport is expected due to acoustic streaming. This will occur even when the sound field is a stable standing wave in the absence of cavitation.[67]

When a liquid-solid interface is subjected to ultrasound, transient cavitation still occurs, but with major changes in the nature of the bubble collapse. No longer does a spherical implosion of the cavity occur, but instead there is a markedly asymmetric collapse which generates a jet of liquid directed at the surface, as seen in the high speed microphotographs taken by Ellis[68,69] and Lauterborn[70] and shown in Figure 6. The tip jet velocities measured by Lauterborn are greater than 100 m/sec. The origin of this jet formation is essentially a shaped-charge effect: the rate of collapse is proportional to the local radius of curvature. As collapse of a bubble near a surface begins, it does so with a slight elliptical asymmetry, which is self-reinforcing, and generates the observed jet[71] as shown in Figure 7. The impingement of this jet can create a localized erosion (and even melting), surface pitting, and ultrasonic cleaning[72,73,74]. A second contribution to erosion created by cavitation involves the impact of shock waves generated by cavitational collapse. The magnitude of such shock waves is thought to be as high as 10^4 atmospheres, which will easily produce plastic deformation of malleable metals.[75] The relative importance of these two effects depends heavily on the specific system under consideration.

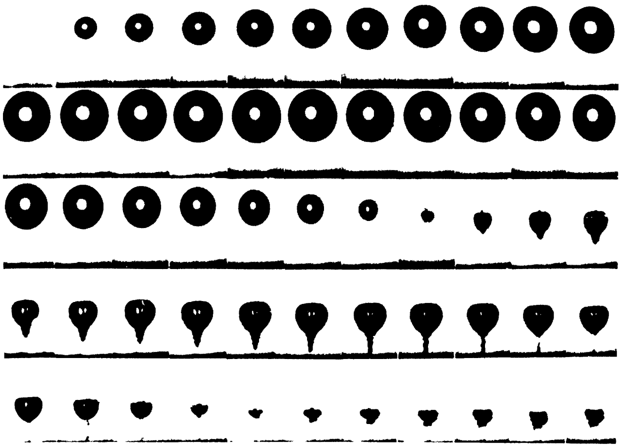


Figure 6. Cavitation Near a Surface. Jet formation from laser-induced cavitation in water at 75,000 frames/sec. Sequence is from left to right, top to bottom; the solid boundary is at the bottom of each frame. [W. Lauterborn[70]]

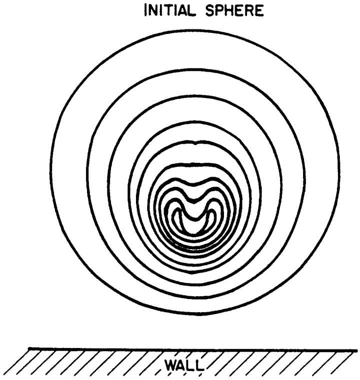


Figure 7. Theoretical Surface Profiles of Collapsing Bubble Near a Boundary. Initially, the distance of the bubble's edge from the boundary was $R_0/2$. [After E. A. Neppiras[24]]

Enhanced chemical reactivity of solid surfaces is associated with these processes. The cavitational erosion generates unpassivated, highly reactive surfaces; it causes short-lived high temperatures and pressures at the surface; it produces surface defects and deformations; it forms fines and increases the surface area of friable solid supports; and it ejects material in unknown form into solution. Finally, the local turbulent flow associated with acoustic streaming improves mass transport between the liquid phase and the surface, thus increasing observed reaction rates. In general, all of these effects are likely to be occurring simultaneously, and in no case of sonochemical activation of solids have their relative contributions been definitively established.

3. EXPERIMENTAL INFLUENCES ON SONOCHEMISTRY

3.1. Reactor Design and Configuration

A variety of devices have been used for ultrasonic irradiation of solutions. There are three general designs in use presently: the ultrasonic cleaning bath, the "cup-horn" sonicator, and the direct immersion ultrasonic horn. In all cases the original source of the ultrasound is a piezoelectric material, usually a lead zirconate titanate ceramic (PZT), which is subjected to a high AC voltage with an ultrasonic frequency (typically 15 to 50 KHz). The piezoelectric source expands and contracts in this electric field and is attached to the wall of a cleaning bath or to an amplifying horn.

The ultrasonic cleaning bath is clearly the most accessible source of laboratory ultrasound and has been used successfully for a variety of liquid-solid heterogeneous sonochemical studies. There are, however, several potential drawbacks to its use. There is no control of the acoustic intensity, which will vary from bath to bath and over the lifetime of a single cleaning bath. In addition, the acoustic frequency is not well-controlled and differs from one manufacturer to another, so that reproducibility from one bath to another may therefore suffer. Reproducible positioning of the reaction flask in the bath is critical, since standing waves in the bath will create nodal spots where cavitation will not occur.[76] Similarly, the height of the bath liquid and of the solution within the reaction vessel are extremely important.[76,77] Temperature control is often neglected with this apparatus. Since the bath temperature can rise >25°C during the course of a long irradiation, this can significantly influence both the intensity of the cavitational collapse and the rate of background thermal reactivity. Thermostating is best done using coolant passed through copper coils suspending in the bath (not in contact with the walls). The temperature inside the reaction vessel must be measured directly since it is often warmer than that in the bath itself. Finally, and most critically, the acoustic intensities present in most cleaning baths are only marginal for the generation of cavitation in homogeneous liquids. When solids are present, the weakened tensile strength of the liquid at the interface will allow cavitation at thresholds well below those of simple solutions. Even in the case of heterogeneous sonochemistry, however, the ultrasonic cleaning bath must be viewed as an apparatus of limited capability.

The cup-horn configuration, shown in Figure 8, was originally designed for cell disruption, but has been adopted for sonochemical studies as well.[78] It has greater acoustic intensities, better frequency control, and potentially better thermostating than the cleaning bath. It too is very sensitive to the liquid levels and to shape of the reaction vessel. In addition, the reaction vessel faces a size restriction of ≈5 cm diameter. Since the ultrasonic radiating surface is not in direct contact with the reaction solution, the acoustic intensities are much lower than those of the direct immersion horn, and so homogeneous sonochemistry is often quite sluggish. On the other hand, there is no possibility of contamination from erosion of the titanium horn.

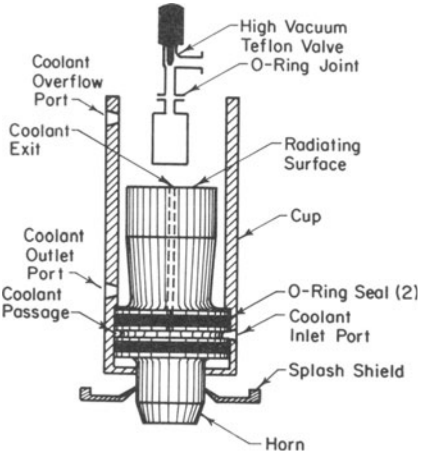


Figure 8. Cup-Horn Sonicator. Modification of a design from Heat Systems-Ultrasonics[78,79]

The most intense source of ultrasound generally used in the chemical laboratory is the direct immersion ultrasonic horn, which we have adapted for inert atmosphere work, as shown in Figure 9, or for moderate pressures (<10 atmospheres). These devices are available from several manufacturers[79] at modest cost and are used primarily by biochemists for cell disruption. A variety of sizes of power supplies and titanium horns are available, thus allowing flexibility in sample size. Commercially available flow-through reaction chambers which will attach to these horns allow the processing of multi-liter volumes. The acoustic intensities are easily and reproducibly variable; the acoustic frequency is well-controlled, albeit fixed (typically at 20 KHz). Since power levels are quite high, counter-cooling of the reaction solution is essential to provide temperature control; cooling of the piezoelectric ceramic may also be necessary, depending on the configuration. One potential disadvantage in corrosive media is the erosion of the titanium tip; this is generally a very slow process without chemical consequences, given the high tensile strength and low reactivity of Ti metal. This configuration may be used for both homogeneous and heterogeneous sonochemistry.

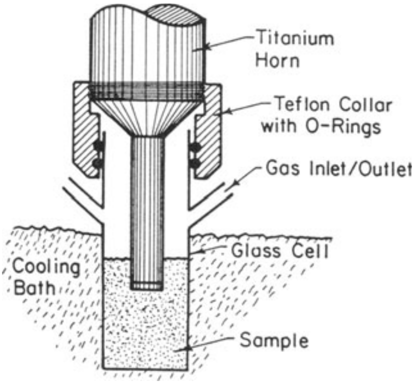


Figure 9. Direct Immersion Ultrasonic Horn Equipped for Inert Atmosphere Work [Design of K. S. Suslick[174]]

A rough, but useful, comparison between typical sonochemical and photochemical efficiencies is shown in Table 1. As shown, homogeneous sonochemistry is typically more efficient than photochemistry, and heterogeneous sonochemistry is several orders of magnitude better. Unlike photochemistry, whose energy inefficiency is inherent in the production of photons, ultrasound can be produced with nearly perfect efficiency from electric power. Still, a primary limitation of sonochemistry remains its energy inefficiency due to small fraction of the acoustic power involved in the cavitation events. This might be significantly improved, however, if a more efficient means of utilizing the sound field to generate cavitation can be found.

Large-scale ultrasonic generation is a well established technology. Liquid processing rates of 200 L/min are routinely accessible from a variety of modular, in-line designs with acoustic power of several KW per unit.[80] The industrial uses of these units include 1) degassing of liquids, 2) dispersion of solids into liquids, 3) emulsification of immiscible liquids and 4) large-scale cell disruption.[61] While these units are of limited use for most laboratory research, they are of potential importance in eventual industrial application of sonochemical reactions.

Table 1

COMPARISONS BETWEEN SONOCHEMICAL AND PHOTOCHEMICAL APPARATUS

	Photochemistry	Homogeneous Sonochemistry	Heterogeneous Sonochemistry
Source	250W Quartz-Halogen	200W Cell Disrupter (at 60% power)	150W Cleaning Bath
Approximate Cost	$1800	$1900	$700
Typical Rates	7 μmol/min	10 μmol/min	500μmol/min
Electrical Efficiency	2 mmol/KWH	5 mmol/KWH	200 mmol/KWH

3.2. Extrinsic Variables

Sonochemistry is strongly affected by a variety of external variables, including acoustic frequency, acoustic intensity, bulk temperature, static pressure, ambient gas, and solvent. These are the important parameters which need consideration in the effective application of ultrasound to chemical reactions. The origin of these influences is easily understood in terms of the hot spot mechanism of sonochemistry. A summary of these effects is given in Table 2.

The frequency of the sound field is surprisingly irrelevant to most sonochemistry. Unlike photochemistry, there is no direct coupling of the irradiating field with the molecular species in sonochemistry. The effect of changing sonic frequency is simply one of altering the resonant size of the cavitation event. The overall chemistry is therefore little influenced over the range where cavitation can occur (from tens of Hz to a few MHz[24]); the observed sonochemical rates may change, but controlled comparisons of efficiency are lacking at this time and will prove difficult. For example, the observed sonochemistry of aqueous solutions is unchanged over this entire range.[81] At very high frequencies (above a few MHz), cavitation ceases, and sonochemistry is generally not observed[82,83,84]. The observed thresholds for cavitation in homogeneous liquids are strongly frequency dependent[6]; since homogeneous sonochemistry is generally studied at acoustic intensities well above the threshold, however, this is not a major concern.

Acoustic intensity has a dramatic influence on the observed rates of sonochemical reactions. Below a threshold value, the amplitude of the sound field is too small to induce nucleation or bubble growth. Above the cavitation threshold, increased intensity of irradiation (from an immersion horn, for example) will increase the effective volume of the zone of liquid which will cavitate, and thus increase the observed sonochemical rate. Furthermore, as the acoustic pressures increase, the range of bubble sizes which will undergo transient cavitation increases (as shown in Figure 3); this too will increase the observed sonochemical rate. It is often observed experimentally, however, that as one continues to increase acoustic amplitude, eventually rates begin to diminish.[85] Possible explanations for this behavior include bubble shrouding of the sonic horn and overgrowth of bubbles. At high intensities, the cavitation of the liquid near the radiating surface becomes so intense as to produce a shroud of bubbles which will diminish the penetration of the sound into the liquid. Also at high intensities, bubble growth may become so rapid that the bubble grows beyond the size range of transient cavitation before implosive collapse can occur.[86]

Table 2

THE EFFECTS OF EXTRINSIC VARIABLES ON SONOCHEMISTRY

Extrinsic Variable	Physical Property	Cavitational Effects
Acoustic Frequency	Period of Collapse	Resonant Bubble Size
Acoustic Intensity	Reaction Zone Size	Cavitation Events per Volume
Bulk Temperature	Liquid Vapor Pressure	Bubble Content, Intensity of Collapse
	Thermal Activation	Enhanced Secondary Reaction Rates
Static Pressure	Total Applied Pressure	Intensity of Collapse
	Gas Solubility	Bubble Content
Ambient Gas	Polytropic Ratio	Intensity of Collapse
	Thermal Conductivity	Intensity of Collapse
	Chemical Reactivity	Primary or Secondary Sonochemistry
	Gas Solubility	Bubble Content
Liquid	Vapor Pressure	Intensity of Collapse
	Surface Tension	Transient Cavitation Threshold
	Viscosity	Transient Cavitation Threshold
	Chemical Reactivity	Primary or Secondary Sonochemistry

The effect of the bulk solution temperature lies primarily in its influence on the bubble content before collapse. With increasing temperature, in general, sonochemical reaction rates are slower! This reflects the dramatic influence which solvent vapor pressure has on the cavitation event: the greater the solvent vapor pressure found within a bubble prior to collapse, the less effective the collapse. In fact, one can quantitate this relationship rather well.[87] A linear correlation of ln k_{obs} and P_v is the experimentally observed behavior in a wide range of sonochemical systems in a variety of solvents.[87,88] When secondary reactions are being monitored (as in secondary corrosion or other thermal chemical reactions occurring after initial acoustic erosion of a passivated surface), temperature will play its usual role in thermally activated chemical reactions. This explains the occasional observation that rates of cavitational corrosion increase as the temperature is increased.[89] Thus, for sonochemical systems which involve secondary thermal reactions, the overall effect of bulk temperature is ambiguous: increased bulk temperature may increase, decrease, or not affect the overall observed rate.

Sonochemical yields as a function of increasing static pressure have been reported by different researchers to increase[4], to decrease[90], and to increase to some point and then decrease[91]. One would expect that cavitational collapse would increase in intensity with increasing external pressure, since the total imposed pressure at the initiation of collapse would be increased. Given a fixed acoustic intensity, however, nucleation of cavities will no longer occur at some point of increasing ambient pressure, since the acoustic field must overcome the combined tensile strength of the liquid and the applied pressure. In contrast, as the ambient pressure is reduced, eventually the gas-filled crevices which serve as nucleation sites (discussed earlier) will be deactivated, and therefore the observed sonochemistry will be diminished. Further experimental difficulties occur when one attempts to maintain a pressure vessel at constant temperature while under ultrasonic irradiation. It is perhaps not surprising, then, that the reported results on the effect of pressure are not in full agreement. In reactions which involve the ambient gas directly, enhanced solubility would also play a role in the overall observed rates.

The choice of ambient gas will also have a major impact on sonochemical reactivity. The maximum temperature reached during cavitation is strongly dependent on the polytropic ratio ($\gamma=C_p/C_v$) of the ambient gas, which defines the amount of heat released during the adiabatic compression of that gas. This can have a dramatic impact: all other factors being equal, cavitation in the presence of xenon ($\gamma=1.67$) versus a freon ($\gamma\approx1.1$), for example, would yield a ratio of maximum temperatures of sevenfold! Sonochemical rates are also significantly influenced by the thermal conductivity of the ambient, so even the noble gases affect cavitation differently.[92,93] The role of thermal transport during cavitational collapse has been long recognized as evidence in favor of the hot-spot mechanism of sonochemistry,[92] and recent calculations underscore its effect on conditions generated during cavitational collapse.[28,29] In addition, sonochemical reactions will often involve the gases present in the cavitation event.[94] For example, H_2, N_2, O_2, and CO_2 are not inert during cavitation and will undergo a variety of redox and radical reactions. Another relevant parameter, gas solubility, has been observed to affect the concentration of cavitation nuclei,[95] and in this way, may play a role in determining the observed cavitation threshold.

The choice of the solvent also has a profound influence on the observed sonochemistry. The effect of vapor pressure has already been mentioned. Other liquid properties, such as surface tension and viscosity, will alter the threshold of cavitation[6], but this is generally a minor concern. The chemical reactivity of the solvent is often much more important. As discussed below, aqueous sonochemistry is dominated by secondary reactions of OH• and H• formed from the sonolysis of water vapor in the cavitation zone. No solvent is inert under the high temperature conditions of cavitation: even linear alkanes will undergo pyrolytic-like cracking during high intensity sonication.[87] One may minimize this problem, however, by using robust solvents (avoiding halocarbons, in particular) which have low vapor pressures so as to minimize their concentration in the vapor phase of the cavitation event. Similarly, one must anticipate secondary solvent reactivity in the trapping of high energy species produced during cavitation.

Thus, the parameters of acoustic intensity, temperature, ambient gas, and solvent choice have strong influences on sonochemical reactions. It is clear that one can fine-tune the energetics of cavitation by the use of these variables, and hence exercise control on the rates and reaction pathways followed by the associated chemistry. Specific examples will be discussed shortly. Clearly, the thermal conductivity of the ambient gas (e.g., a variable He/Ar atmosphere) and the overall solvent vapor pressure provide easy methods for the experimental control of the peak temperatures generated during the cavitational collapse.

4. SYNTHETIC APPLICATIONS OF ULTRASOUND

4.1. Homogeneous Systems

The effects of high-intensity ultrasound on chemical systems is an area of only limited, and in large part recent, investigation; consequently, a limited range of reactions have been examined. Still, a variety of novel reactivity patterns are beginning to emerge which are distinct from either normal thermal or photochemical activation. Most of the reactions which have been reported are stoichiometric in terms of a consumed reagent, but a few examples of true sonocatalysis have also appeared. Although there is some overlap, we will divide our discussion into homogeneous and heterogeneous systems, in part because of the distinct nature of the cavitation event in each case.

4.1.1. Aqueous Sonochemistry

The sonolysis of water[1,91,94,96,97,98,99,100,101,102,103] has been exhaustively studied. The first observations on the experimental parameters which influence sonochemistry come from these reports. The primary products are H_2O_2 and H_2, and various data supported their formation from the intermediacy of hydroxyl radicals and hydrogen radicals:

$$H_2O \text{ -)-)-)}\!\rightarrow OH\cdot + H\cdot \longrightarrow H_2O_2 + H_2 \qquad [1]$$

Spin trapping experiments[104] have recently provided the final definitive evidence for the intermediacy of $OH\cdot$ and $H\cdot$, but data have also suggested the formation of a variety of other high energy species, depending on conditions (ambient gas, pH, etc.), including $e^-_{(aq)}$[105] and $HO_2\cdot$.[106]

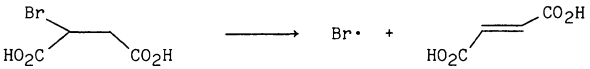
Given the facile homolytic cleavage of water during ultrasonic irradiation, a wide range of secondary sonochemistry in aqueous solutions would be expected and indeed have been repeatedly observed. The sonochemical oxidations and reductions of inorganic species have been extensively studied, but are beyond this review.[107,108,109,110,111,112,113,114,115,116,117,118]

Various organics have been sonicated either as aqueous solutions or suspensions, and are compiled in Table 3. Aqueous sonochemistry of organic compounds usually results in the generation of a large number of highly oxidized or degraded products. Since extremely reactive intermediates are formed at respectable rates from the sonolysis of water itself, it is not surprising to see a general lack of specificity for sonochemistry in aqueous media. If we consider the nature of the cavitation event, the high vapor pressure of water, relative to inorganic species or to dilute organic compounds, condemns aqueous sonochemistry to be dominated by secondary chemical reactions unrelated to the direct processes which such dissolved substrates might undergo had they been the major species found in the collapsing bubble.

The sonochemical stereoisomerization of maleic acid to fumaric acid in the presence of Br_2 or some bromocarbons is an interesting exception. This is a general reaction independent of the frequency of sound used over a very wide range.[119] This reaction is an unusual example of sonocatalysis, since the Br· formed from sonolysis is a competent catalyst for the isomerization, as shown below.

$$Br_2 \longrightarrow 2\,Br\cdot \qquad [2]$$

[3]



[4]

A number of reports on the effects of ultrasound on various solvolysis reactions have appeared. The first of these[120], in addition to finding rate enhancements for the hydrolysis of acetates and saponification of fats, also found that acoustic cavitation caused sake, shoyu (soy sauce), and whisky to mellow rapidly! More recently, detailed studies have been carried out on the solvolysis of 2-chloro-2-methylpropane in aqueous alcoholic media.[50,51,52,53] The rate enhancements have generally been quite small (<50%) at room temperature, but increase sharply with decreasing temperature. Apparent activation parameters have been measured as a function of alcohol concentration, but the effects of solvent vapor pressure have not been included in this analysis, which precludes unambiguous interpretation of the origin of these rate enhancements.

Table 3

AQUEOUS SONOCHEMISTRY OF ORGANIC COMPOUNDS

Substrate Present	Principal Products	References
CCl_4	Cl_2, CO_2, HCl, C_2Cl_6, HOCl	40,98,121,122,123
CH_3I	CH_4, I_2, CH_3OH, HI, C_2H_6	124
R_2CHCl	R_2CHOH, HCl	50,51,52,53
$Cl_3CCH(OH)_2$	HCl	125,126
C_6H_5Br	Br^-, C_2H_2	127,128
maleic acid + Br_2	fumaric acid	129,130
CS_2	S, H_2S	131
$(C_4H_9)_2S$	$(C_4H_9)_2SO$, polymer	132
RCHO	CO, CH_4, C_2H_4, $C_2H_4O_2$, RCO_2H	133
HCO_2^-	CO_2	134
C_5H_5N	HCN, C_2H_2, C_4H_2	128,135
C_6H_5OH	$C_6H_4(OH)_2$	136
$C_6H_5CO_2H$	$C_6H_4(OH)(CO_2H)$	137
$C_6H_{11}OH$	C_2H_2	138
RCO_2H	CO, CH_4	133
RCO_2R'	RCO_2H, R'OH	49,120,139,140,141,142
RCH_2NH_3	H_2, CH_4, NH_3, RCHO, RCH_2OH	143
$(CH_2NH_2)_2$	NH_3	118
thymine	hydroxylated products	5,144,145
uracil	hydroxylated products	5,146,147
various amino acids	H_2, CO, NH_3, RNH_2, HCHO	148
cysteine	cystine	148
$C_6H_5CHCH_2$	polymerization	149
$H_2CC(CH_3)(CO_2H)$	polymerization	150
$H_2CCH(CONH_2)$	polymerization	151
many polymers	depolymerization	48

4.1.2. Non-Aqueous Sonochemistry

4.1.2.1. Neat Liquids

Until the past few years, very few examples of homogeneous non-aqueous sonications had been reported. These included the very slow degradation of a few common solvents[152] (CH_3CN and CCl_4), the initiation of explosions of tetranitromethane and nitroglycerine[153], the sevenfold acceleration[154] of the Curtius rearrangement of $C_6H_5CON_3$ to C_6H_5NCO and N_2, and the depolymerization of high molecular weight polymers[48]. In general, sonochemistry had not been observed in most common, volatile organic solvents (or aqueous solutions with volatile organics). This led to the commonly stated assumption that intense cavitational collapse could only be supported in high tensile strength liquids such as water.[155,156] As noted earlier, however, the problem is simply that many organic liquids have high vapor pressures, which greatly diminish the intensity of cavitational collapse.

It is now clearly demonstrated through the use of free radical traps that all organic liquids will undergo cavitation and generate bond homolysis, if the ambient temperature is sufficiently low (i.e., in order to reduce the solvent system's vapor pressure).[87,88,157,158] The sonolysis of alkanes is quite similar to very high temperature pyrolysis, yielding the products expected (H_2, CH_4, 1-alkenes, and acetylene) from the well-understood Rice radical chain mechanism.[87] Other recent reports compare the sonolysis and pyrolysis of biacetyl (which gives primarily acetone)[159], and the sonolysis and radiolysis of menthone.[160] Non-aqueous chemistry can be complex, however, as in the tarry polymerization of several substituted benzenes.[161,162,163,164]

In general, the examination of sonochemical reactions in aqueous solutions has produced results difficult to interpret due to the complexity of the secondary reactions which so readily occur. However, by the proper choice of solvent and experimental conditions (low volatility, highly stable liquids at low temperature: e.g., decane, -10°C) the rates of degradation of non-aqueous liquids can be made quite slow, well below those of water. This is of considerable advantage, since the primary sonochemistry of dissolved substrates can then be examined, rather than their secondary reactions with solvent fragments. One may hope to see the increased use of low-volatility organic liquids in future sonochemical studies.

4.1.2.2. Stoichiometric Reactions

In 1981, the first report on the sonochemistry of discrete organometallic complexes demonstrated the effects of ultrasound on the iron carbonyls in alkane solutions.[165] The transition metal carbonyls were chosen for these initial studies because their thermal and photochemical reactivities have been well-characterized. The comparison among the thermal, photochemical, and sonochemical reactions of $Fe(CO)_5$ provides an excellent example of the unique chemistry which homogeneous cavitation can induce. Because of the mechanistic insights which this system has provided, we will focus upon it as an archetype. Thermolysis of $Fe(CO)_5$, for example, gives pyrophoric, finely divided iron powder;[166] ultraviolet photolysis[167] yields $Fe_2(CO)_9$, via the intermediate $Fe(CO)_4$; multiphoton infrared photolysis in the gas-phase[168,169] yields isolated Fe atoms. Multiple ligand dissociation, generating $Fe(CO)_3$, $Fe(CO)_2$, etc., is not available from ordinary thermal or photochemical processes (but does occur in matrix isolated[170,171] and gas phase laser[172,173] photolyses). These observations reflect the dual difficulties inherent in creating controlled multiple ligand dissociation: first, to deliver sufficient energy in a utilizable form and, second, to quench the highly energetic intermediates before complete ligand loss occurs.

Sonolysis of $Fe(CO)_5$ in alkane solvents in the absence of alternate ligands causes the unusual clusterification to $Fe_3(CO)_{12}$, together with the formation of finely divided iron.[165,174] The rate of decomposition is cleanly first order, and the log of the observed first order rate coefficient is linear with the solvent vapor pressure. This is consistent with a simple dissociation process activated by the intense local heating generated by acoustic cavitation. As discussed earlier, the intensity of the cavitational collapse and the maximum temperature reached during such collapse decreases with increasing solvent vapor pressure. Thus, we would also expect to see the ratio of products vary as a function of solvent vapor pressure. This proves to be the case: the ratio of products can be varied over a 100-fold range, with the production of $Fe_3(CO)_{12}$ strongly favored by increasing solvent volatility, as expected, since the sonochemical production of metallic iron requires greater activation energy than the production of $Fe_3(CO)_{12}$

The proposed chemical mechanism by which $Fe_3(CO)_{12}$ is formed during the sonolysis of $Fe(CO)_5$ is shown in Equations 6 - 9.

$$Fe(CO)_5 \text{ -)-)-)}\!\rightarrow Fe(CO)_{5-n} + n\ CO \quad (n=1-5) \qquad [5]$$

$$Fe(CO)_3 + Fe(CO)_5 \longrightarrow Fe_2(CO)_8 \qquad [6]$$

$$2\ Fe(CO)_4 \longrightarrow Fe_2(CO)_8 \qquad [7]$$

$$Fe_2(CO)_8 + Fe(CO)_5 \longrightarrow Fe_3(CO)_{12} + CO \qquad [8]$$

$Fe_2(CO)_9$ is not generated during the synthesis of $Fe_3(CO)_{12}$, and sonolysis of $Fe_2(CO)_9$ yields only $Fe(CO)_5$ and finely divided iron. The production of

$Fe_3(CO)_{12}$ arises from initial multiple dissociative loss of CO from $Fe(CO)_5$ during cavitation, followed by secondary reactions with excess $Fe(CO)_5$. Ligand trapping studies confirm the formation of $Fe(CO)_3$, but cannot rule out the dimerization of $Fe(CO)_4$ in the localized cavitation site. The reaction of the putative $Fe_2(CO)_8$ with $Fe(CO)_5$ may proceed through initial dissociation in analogy to the matrix isolation reactivity[175] of $Fe(C_4H_4)_2(CO)_4$.

In the presence of added Lewis bases, sonochemical ligand substitution also occurs for $Fe(CO)_5$, and in fact for most metal carbonyls. This has proved useful as a mechanistic probe of the reactive species formed during cavitation. Sonication of $Fe(CO)_5$ in the presence of phosphines or phosphites produces $Fe(CO)_{5-n}L_n$, n=1, 2, and 3. The ratio of these products is independent of length of sonication; the multiply substituted products increase with increasing initial [L]; $Fe(CO)_4L$ is not sonochemically converted to $Fe(CO)_3L_2$ on the time scale of its production from $Fe(CO)_5$. These observations are consistent with the same primary sonochemical event responsible for clusterification:

$$Fe(CO)_5 \;-)-)-)\!\rightarrow\; Fe(CO)_{5-n} + n\,CO \quad (n=1-5) \qquad [9]$$

$$Fe(CO)_4 + L \longrightarrow Fe(CO)_4L \qquad [10]$$

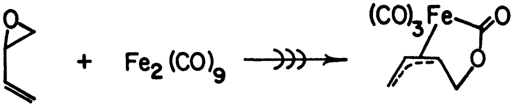
$$Fe(CO)_3 + L \longrightarrow Fe(CO)_3L \qquad [11]$$

$$Fe(CO)_3 + CO \longrightarrow Fe(CO)_4 \qquad [12]$$

$$Fe(CO)_3L + L \longrightarrow Fe(CO)_3L_2 \qquad [13]$$

Sonochemical ligand substitution readily occurs with a variety of other metal carbonyls, as shown in Table 4. In all cases, multiple ligand substitution originates directly from the parent carbonyl. The rates of sonochemical ligand substitution of the various metal carbonyls follow their relative volatilities, as predicted from the nature of the cavitational collapse.

Another recent example of sonochemical substitution is in the preparation of π-allyllactone(tricarbonyl)iron complexes, which are useful synthetic intermediates in the synthesis of lactones and lactams.[176] Upon sonication in a cleaning bath, $Fe_2(CO)_9$ slurries in hydrocarbon solutions of alkenyl epoxides rearrange as shown:



[14]

The same reaction occurs thermally with $Fe(CO)_4$(tetrahydrofuran), indicating the probable intermediacy of a coordinatively unsaturated (or loosely coordinated) species upon sonication of $Fe_2(CO)_9$. The authors expressed surprise[176] that under their conditions $Fe(CO)_5$ and $Fe_3(CO)_{12}$ did not undergo the same reaction, in light of the similarity in their sonocatalytic behavior and their sonochemical substitution with phosphines.[174] This is clearly due, however, to the low intensities of ultrasound present in these authors' ultrasonic cleaning bath, which are sufficient to induce cavitation in the heterogeneous slurries of $Fe_2(CO)_9$, but which are <u>not</u> sufficient in homogeneous solutions of $Fe(CO)_5$ or $Fe_3(CO)_{12}$. Under more intense ultrasonic irradiation, $Fe(CO)_5$, for example, will undergo substitution with alkenes.[174]

The sonolysis of $Mn_2(CO)_{10}$ makes for an interesting comparison,[177] since either metal-metal (as in photolysis)[178] or metal-carbon (as in moderate-temperature thermolysis)[179] bond breakage could occur. Ligand substitution will occur from all of these routes to produce the axially disubstituted $Mn_2(CO)_8L_2$. Using benzyl chloride as a trap for the intermediacy of $Mn(CO)_5\cdot$, the sonochemical substitution of $Mn_2(CO)_{10}$ has been shown to follow the thermal, rather than the photochemical, pathway of dissociative CO loss.

Upon sonication in halocarbon solvents, metal carbonyls undergo facile halogenations.[177] The rates of halogenation are solvent dependent, but independent of choice of metal carbonyl or its concentration, and represent the products of secondary reactions occurring from the sonolytic decomposition of the halocarbon solvent, as shown below. Alkanes and other halogen

$$R_3CX \text{ -)-)-)}\!\rightarrow R_3C\cdot + X\cdot \qquad [15]$$

$$2\ R_3C\cdot \longrightarrow R_3CR_3 \qquad [16]$$

$$2\ X\cdot \longrightarrow X_2 \qquad [17]$$

$$M_2(CO)_{10} + 2\ X\cdot \longrightarrow 2\ M(CO)_5X \qquad [18]$$

$$M_2(CO)_{10} + X_2 \longrightarrow 2\ M(CO)_5X \qquad [19]$$

atom traps suppress the halogenation of the metal carbonyls.

Another example of a secondary sonochemical reaction is the very slow production of acetylene complexes of cobalt carbonyls upon lengthy sonolysis of $Co_2(CO)_8$ in n-alkanes (C_5H_{12} through $C_{10}H_{22}$).[180] The principal products are $Co_2(CO)_6(H_2C_2)$ and $Co_4(CO)_{10}(H_2C_2)$ and small amounts of $Co_4(CO)_{12}$. $Co_4(CO)_{12}$ is an expected product, since it is easily formed upon pyrolysis of $Co_2(CO)_8$. The acetylene of the former complexes originates from the solvent, as confirmed by isotope labelling. The sonochemical synthesis of these complexes is initially quite surprising, until one notes that their rates of formation are comparable to the slow rate of H_2C_2 formation from sonolysis of the alkane,[87] and that cobalt carbonyls undergo facile thermal reactions with alkynes[181]. Thus, the origin of this sonochemical alkane activation is <u>not</u> from some high energy organometallic fragment, but from the secondary trapping of acetylene sonochemically produced from the alkane.

The sonochemistry of non-carbonyl organometallics has not yet been well-developed. Complexes which contain both CO and Cp undergo CO substitution upon sonolysis.[180] In preliminary studies of the metallocenes,[182] $Co(Cp)_2$ has been found to undergo facile ligand substitution during sonication under CO to yield $Co(Cp)(CO)_2$. This reaction under simple thermal conditions[183] requires 200 atmospheres CO at 90-150°C and gives low yields; with ultrasonic irradiation, excellent yields are obtained at 3 atmospheres and 20°C. These results are in keeping with the high temperature and pressure conditions generated during acoustic cavitation, and suggest an analogy between sonochemistry and bomb reactions.

A recent report describes the sonochemical decomposition of organotin compounds.[184] Trapping of intermediate radicals by nitrosodurene and analysis by ESR demonstrated alkyl-tin bond cleavage during sonication in benzene solutions. The following reaction scheme was suggested to explain the observed ESR spectra. The yields, rates, source of oxidant, or final products in the absence of spin traps were not determined.

$$R_4Sn \;-)-)-)\!\rightarrow\; R\cdot + R_3Sn\cdot \qquad [20]$$

$$R\cdot + ONC_6H(CH_3)_4 \longrightarrow \cdot ON(R)(C_6H(CH_3)_4) \qquad [21]$$

$$R_3Sn\cdot + C_6H_6 \longrightarrow R_3SnC_6H_6\cdot \qquad [22]$$

$$R_3SnC_6H_6\cdot + ONC_6H(CH_3)_4 + ox \longrightarrow \cdot ON(C_6H_4SnR_3)(C_6H(CH_3)_4) + rd \qquad [23]$$

Table 4

HOMOGENEOUS ORGANOMETALLIC SONOCHEMISTRY

Reactants	Products	References
Clusterification:		
$Fe(CO)_5$	$Fe_3(CO)_{12}$, Fe	165,174
$Fe_2(CO)_9$	Fe, $Fe(CO)_5$	165,174
Ligand Substitution:*		
$Cr(CO)_6 + L$	$Cr(CO)_5L$, $Cr(CO)_4L_2$, $Cr(CO)_3L_3$	174
$M(CO)_6 + L$ (M=Mo,W)	$Mo(CO)_5L$, $Mo(CO)_4L_2$	174
$Fe(CO)_5 + L$	$Fe(CO)_4L$, $Fe(CO)_3L_2$, $Fe(CO)_2L_3$	165,174
$FeCp(CO)_2I + L$	FeCp(CO)(L)I	180
$Fe_2(CO)_9$ + alkenylepoxide	$Fe(CO)_3$(π-allyllactone)	176
$Fe_3(CO)_{12} + L$	$Fe(CO)_4L$, $Fe(CO)_3L_2$	165,174
$Mn_2(CO)_{10} + L$	$Mn_2(CO)_8L_2$	177
$Co(Cp)_2 + CO$	$CoCp(CO)_2$	182
Sn_2R_6	$SnR_3\cdot$, $R\cdot$	184
Secondary Reactions:		
$M_2(CO)_{10} + R_3CX$	$M(CO)_5X$ (M=Mn, Re; X=Cl,Br)	177
$Co_2(CO)_8$ + alkane	$Co_2(CO)_6(C_2H_2)$, $Co_4(CO)_{10}(C_2H_2)$	180
Sonocatalytic Reactions:		
$Fe_x(CO)_y$ + 1-alkene	cis-, trans-2-alkene	165,174
$Ru_x(CO)_y$ + 1-alkene	cis-, trans-2-alkene	174
$Mo(CO)_6$ + 1-alkene	cis-, trans-2-alkene	174
$Co_2(CO)_8$ + 1-alkene	cis-, trans-2-alkene	174

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* L = various phosphines and phosphites.

4.1.2.3. Initiation of Homogeneous Catalysis

Having demonstrated that ultrasound can induce ligand dissociation, the initiation of homogeneous catalysis by ultrasound becomes practical. The potential advantages of such sonocatalysis include 1) the use of low ambient temperatures to preserve thermally sensitive substrates and to enhance selectivity, 2) the ability to generate high-energy species unobtainable from photolysis or simple pyrolysis, 3) the mimicry, on a microscopic scale, of bomb reaction conditions, and 4) possible ease of scale-up. The transient, coordinatively unsaturated species produced from the sonolysis of metal carbonyls are likely candidates, since similar species produced photochemically are among the most active catalysts known.[167,185]

A variety of metal carbonyls upon sonication will catalyze the isomerization of 1-pentene to <u>cis</u>- and <u>trans</u>-2-pentene.[174] Initial turnover rates are ≈1-100 mol 1-pentene isomerized/mol of precatalyst/h, and represent rate enhancements of $\approx 10^5$ over thermal controls.[165] The relative sonocatalytic and photocatalytic activities of these carbonyls are in general accord. An exception is $Ru_3(CO)_{12}$, which is relatively more active as a sonocatalyst and shows very different <u>trans</u>/<u>cis</u> ratios under sonolysis; it appears that the catalytic agent produced sonochemically in this case is not that produced photochemically. A variety of terminal alkenes will serve as substrates for sonocatalytic isomerization, although increasing steric hindrance, as in 2-ethylpent-1-ene and allylbenzene, significantly diminishes the observed rates. Alkenes without β-hydrogens will not serve as substrates.

The exact nature of the catalytic species generated during sonolysis remains unknown. Results are consistent with the generally accepted mechanism for alkene isomerization in analogous thermal[186,187,188] and photochemical systems.[189,190] This involves the formation of a hydrido-π-allyl intermediate and alkene rearrangement via hydride migration to form the thermodynamically more stable 2-alkene complex, as shown in a general sense in Equations 25-29.

$$\mathrm{M(CO)_n} \longrightarrow \mathrm{M(CO)_m} + \text{n-m CO} \qquad [24]$$

$$\mathrm{M(CO)_m} + \text{1-alkene} \longrightarrow \mathrm{M(CO)_x}(\text{1-alkene}) + \text{m-x CO} \qquad [25]$$

$$\mathrm{M(CO)_x}(\text{1-alkene}) \longrightarrow \mathrm{M(CO)_x(H)}(\pi\text{-allyl}) \qquad [26]$$

$$\mathrm{M(CO)_x(H)}(\pi\text{-allyl}) \longrightarrow \mathrm{M(CO)_x}(\text{2-alkene}) \qquad [27]$$

$$\mathrm{M(CO)_x}(\text{2-alkene}) + \text{1-alkene} \longrightarrow \mathrm{M(CO)_x}(\text{1-alkene}) + \text{2-alkene} \qquad [28]$$

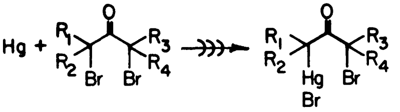
In keeping with this scheme, sonication of $Fe(CO)_5$ in the presence of 1-pentene and CO does produce Fe(CO)$_4$(pentene), as determined by FTIR spectral stripping.[174]

4.2. Heterogeneous Systems

The use of ultrasound to accelerate chemical reactions in heterogeneous systems is becoming increasingly widespread. The physical phenomena which are responsible include the creation of emulsions at liquid-liquid interfaces, the generation of cavitational erosion and cleaning at liquid-solid interfaces, the production of shock wave damage and deformation of solid surfaces, the enhancement in surface area from fragmentation of friable solids, and the improvement of mass transport from turbulent mixing and acoustic streaming.

4.2.1. Liquid-Liquid Systems

One of the major industrial applications of ultrasound is emulsification. This feature may be expected to be of some use in reactions involving two immiscible liquid phases. The first reported and most studied liquid-liquid heterogeneous systems have involved ultrasonically dispersed mercury. The emulsification of Hg with various liquids dates to the very first studies of the chemical effects of ultrasound.[1,191,192] The use of such emulsions for chemical purposes, however, was delineated by the extensive investigations of Fry and coworkers,[193,194,195,196,197,198,199,200] who have reported the sonochemical reaction of various nucleophiles with α,α'-dibromoketones and mercury. The versatility of this reagent is summarized in Equations 29-35:



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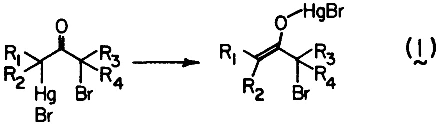

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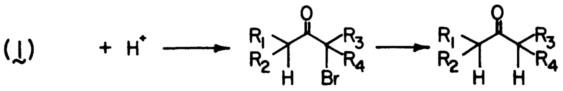

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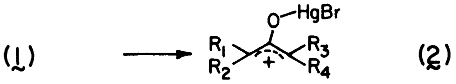

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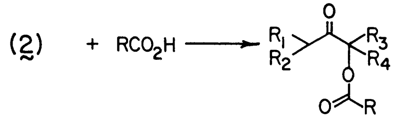

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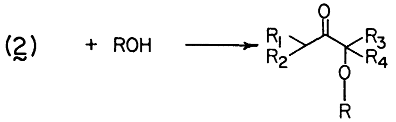

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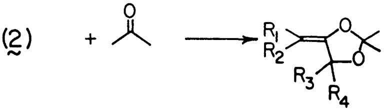


[35]

There are significant synthetic advantages to the use of ultrasound in these systems. For example, such Hg dispersions will react even with quite sterically hindered ketones, yet will introduce only one nucleophilic group even in sterically undemanding systems.[197] In addition, the reaction given in Equation 36 represents a convenient one-step synthesis of 1,3-dioxolans.[194] The proposed mechanism of these reactions involves nucleophilic attack on the mercurial oxyallyl cation, (2). Fry believes that the effect of the ultrasound in this system is a kinetic rate enhancement,[193] presumably due to the large surface area of Hg generated in the emulsion. Another reduction carried out in excellent yield by ultrasonically dispersed Hg is shown in Equation 37; the mechanism by which this occurs is unclear, particularly since no thiobenzaldehyde or 1,2-diphenylthiirane is formed.[200] One might speculate

$$C_6H_5(H)(Br)CSC(Br)(H)C_6H_5 + Hg \longrightarrow \underline{t}\text{-}C_6H_5(H)C{=}C(H)C_6H_5 \qquad [36]$$

that an internal Wurtz coupling is the initial step, forming 1,2-diphenylthiirane, which is rapidly desulfurized to *trans*-stilbene.

Ultrasonic agitation of biphasic aqueous-organic liquid systems has been used in place of phase transfer catalysts in several organic transformations. The *in situ* preparation of dichlorocarbene from aqueous NaOH over $CHCl_3$ has proved especially useful for the dichlorocyclopropanation of alkenes.[201] Using an ultrasonic cleaning bath, in addition to mechanical stirring, isolated yields of the dichlorocyclopropanes were generally above 80% after a few hours at ≈35°C. The selectivity of this process is very similar to $KOC(CH_3)_3/CHCl_3$ at −15°C. The avoidance of phase transfer catalysts or other organic phase soluble salts greatly simplifies workup. Another example of the effect of ultrasound on a aqueous-nonaqueous reaction is the base hydrolysis of nitriles to carboxylates, which leads to moderate rate enhancements and improvements in yields.[202]

An interesting case of the combined use of photochemistry and sonochemistry has appeared recently.[203,204] The pair of immiscible liquids in this case are methyl disulfide and hexafluorobutadiene. Ultraviolet photolysis of CH_3SSCH_3 produces $CH_3S\cdot$, which in the absence of sonication has no access to the hexafluorobutadiene. Using a cup-horn ultrasonic bath during the photolysis, however, gave undisclosed amounts of trans-1,4-bis(methylthio)-hexafluoro-2-butene. No comparison to the photolysis of the two phase system in the presence of mechanical stirring was reported.

4.2.2. Liquid-Solid Reactions

4.2.2.1. Non-Organometallic Reagents

Along the same lines, several papers have appeared in which ultrasonic irradiation of liquid-solid reactions was used to enhance rates and yields. Most of these deal with reactive metals, such as Li, Mg, or Zn, as discussed later. The phenomenon is quite general, however, and ultrasonic rate enhancements for many heterogeneous reagents which are not organometallic also occurs, as summarized in Table 5. Although most of these reports have been made only during the past three years, the first such use dates to 1966, when it was discovered that the deprotonation of dimethylsulfoxide by NaH slurries to form solutions of $Na[H_2CSO(CH_3)]$ was quite conveniently done under high intensity ultrasonic irradiation.[205] The same procedure has recently been used to take dimethylsulfoxide solutions of isoquinoline to 1-methylisoquinoline in high yield.[206]

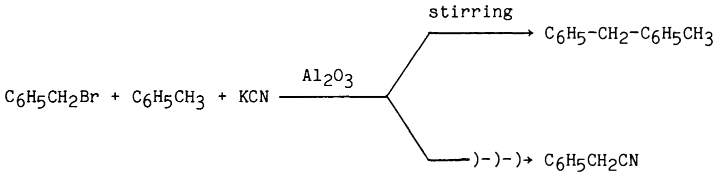
The preparation of thioamides from amides treated with solid P_4S_{10} is also significantly improved upon irradiation in an ultrasonic cleaning bath.[207] The rate enhancement is allows the use of much lower temperatures (≈35°C), for much less time, with much less excess of reagent, and with isolated yields of ≈85%. Similarly, the reduction of aryl halides to arenes with solid lithium aluminum hydride proceeds with very high yields in a few hours with the use of an ultrasonic cleaning bath.[208] This is particularly dramatic with deactivated substrates, like p-bromoanisole or p-bromotoluene, which give poor yields (<20%) of the parent arene in the absence of ultrasound, but which give >80% yields in its presence. In the same vein, the use of low intensity ultrasound for the preparation of main group hydrides from the reaction of the

$$R_3M\text{-}X + LiAlH_4 \ {-)\!-)\!-)\!\rightarrow}\ R_3M\text{-}H \quad (M{=}Si,Ge,Sn;\ X{=}Cl,NR_2,OR) \qquad [37]$$

corresponding chlorides with lithium aluminum hydride has been recently reported.[209] The oxidation of alcohols to ketones or aldehydes with solid

$KMnO_4$ is another example of the same theme.[210] Yields in benzene or hexane are typically >80% under ultrasonic irradiation, but less than 10% in its absence. Rate enhancement of N-alkylation of amines with alkyl halides in the presence of KOH solid and phase transfer catalysts in toluene under ultrasonic irradiation have also been reported.[211] Improvements in yields (typically ≈50% with mechanical stirring and ≈90% with ultrasonic irradiation) and reaction rates (>10 fold) have been observed.

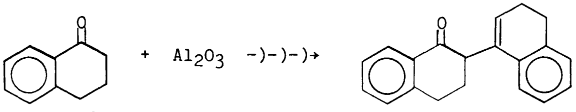
A surprising observation has been made on the effects of ultrasound on the synthesis of aromatic acyl cyanides from acid chlorides and solid KCN in acetonitrile.[212] The extension of this reaction to benzyl bromides led to an unusual, and unexplained, observation of reaction pathway switching:[213] during ultrasonic irradiation in aromatic solvents, benzyl bromide, KCN, and alumina yields benzyl cyanide; whereas with mechanical agitation one obtains diarylmethane products from Friedel-Crafts attack on the solvent. Apparently, the sonication is deactivating the Lewis acid sites normally present on the alumina which are responsible for the Friedel-Crafts reactivity.



$$C_6H_5CH_2Br + C_6H_5CH_3 + KCN \xrightarrow{Al_2O_3} \begin{cases} \xrightarrow{\text{stirring}} C_6H_5\text{-}CH_2\text{-}C_6H_5CH_3 \\ \text{)-)-)}\rightarrow C_6H_5CH_2CN \end{cases}$$

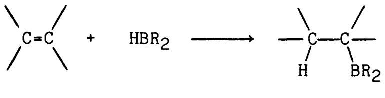
[38]

Another use of alumina under ultrasonic irradiation is as a catalyst for aldol condensations. Substantial improvements in yields were observed, with greatly diminished reaction times, for several ketones.[214]



[39]

The effects of ultrasound on hydroboration have also been explored recently.[215] Particularly with heterogeneous reactions to produce bulky boranes, rate enhancements are quite large and give nearly quantitative yields.



$$>C{=}C< \; + \; HBR_2 \longrightarrow -\underset{H}{C}-\underset{BR_2}{C}-$$

[40]

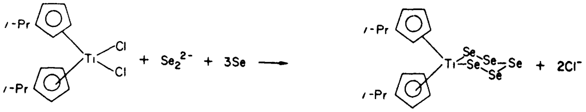
For example, the synthesis of "alpine-borane," a useful chiral reagent for the asymmetric reduction of various prochiral carbonyls, which is normally prepared by the hydroboration of resolved α-pinene with 9-borabicyclo[3.3.1]nonane (9-

BBN) in tetrahydrofuran at 65°C for 12 h, required only 1 h at 25°C with the use of an ultrasonic cleaning bath.

Finally, ultrasound has been used to enhance the rates of mass transport near electrode surfaces, and thus to enhance rates of electrolysis.[216] This has found recent application in the electroreduction of polychlorinated biphenyls[217] and of chalcogens[218]. The latter has some rather useful synthetic applications for the production of both organic and inorganic chalcogenides. The electrochemical reduction of insoluble Se or Te powder by a carbon cloth electrode in the presence of low intensity ultrasonic irradiation produces sequentially E_2^{-2} and E^{-2} (where E is either Se or Te). With generally high current efficiency, these species can be used in a variety of interesting reactions:

$$2E \ \overset{+2e^-}{-)-)-)\!\rightarrow}\ E_2^{-2} \xrightarrow{+2RX} REER + 2X^- \qquad [41]$$

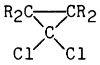
$$E \ \overset{+2e^-}{-)-)-)\!\rightarrow}\ E^{-2} \xrightarrow{+2RX} RER + 2X^- \qquad [42]$$



[43]

Table 5

HETEROGENEOUS NON-ORGANOMETALLIC SONOCHEMISTRY

HETEROGENEOUS REAGENT	ORGANIC REACTANT	PRODUCT	REFERENCES
$LiAlH_4$	Ar-X	ArH	208
$LiAlH_4$	R_3M-X (X=Cl, NR_2, OR)	R_3M-H (M=Si, Ge, Sn)	209
NaH	$(CH_3)_2SO$	$Na^+[H_2CSO(CH_3)]^-$	205
$NaH/(CH_3)_2SO$	isoquinoline	1-methylisoquinoline	206
NaOH (aq. soln.)	$CHCl_3 + R_2C=CR_2$		201
NaOH (aq. soln.)	RCN	RCO_2H	202
KOH	$NHR_2 + R'X$	NR_2R'	211
KCN	ArCOX	ArCO(CN)	212
KCN	Ar-Br (+Al_2O_3)	ArCN	213
$KMnO_4$	RR'HCOH	RR'CO	210
HBR_2	$R'_2C=CR'_2$	$HR'_2C-CR'_2(BR_2)$	215
Al_2O_3	$RCOCH_2R'$	RCOCH(R')(CR=CHR')	214
P_4S_{10}	R_2NCOR'	R_2NCSR'	207
Se, Te (+e^-)	RX	RE_nR (E=Se, Te; n=1, 2)	218
$CH_3SSCH_3 + h\nu$	$F_2C=CFCF=CF_2$	t-$(CH_3S)F_2CCF=CFCF_2(SCH_3)$	203,204

4.2.2.2. Reactive Metals (d^0, d^{10})

The effects of ultrasound on liquid-solid heterogeneous organometallic reactions has been a matter of intense recent investigation and is summarized in Table 6. The first use of ultrasound to prepare organometallic complexes of the main group metals (e.g. lithium, magnesium, and aluminum) from organic halides, however, originates in the seldom cited work of Renaud.[219] Grignard reagents and organolithium compounds were formed rapidly, even in wet solvents, from organobromides (but not chlorides), and Al powder reacted with RMgX without the need for Al-Mg alloys. Renaud also found that such enhancements were not observed for Ca, Hg, Zn (but see below), or Be. This approach has found recent use[220] in the preparation of allyl Grignard reagents, which are prone to undesired side reactions. The activation of Mg by ultrasonic irradiation of Mg in the presence of anthracene[221] (discussed later in detail) was found to be considerably easier than comparable dispersions produced by K reduction of $MgBr_2$.

The report by Luche and Damiano in 1980 of the use of an ultrasonic cleaner to accelerate lithiation reactions[222] initiated the recent interest. Excellent yields of organolithium compounds were found for n-propyl-, n-butyl- and phenyllithium (61-95%), even at room temperature in wet solvents,

$$\text{R-Br} + \text{Li} \longrightarrow \text{R-Li} \qquad \text{R} = \text{Pr, n-Bu, Ph} \qquad [44]$$

which has potential utility for large-scale industrial applications. Lithiation of <u>iso</u>-propyl and <u>tert</u>-butyl bromides remained sluggish, however.

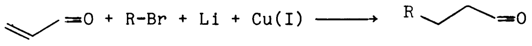
More impressive is the striking improvement which sonication afforded to the Barbier reaction.[222] This one-step coupling of organic halides with

$$\text{R-Li} + \text{R'R''CO} \longrightarrow \text{RR'R''COH} \qquad [45]$$

carbonyl compounds via magnesium or lithium intermediates is significantly hastened with excellent yields (76-100%) for a wide range of organobromides (including <u>tert</u>-butyl and benzyl) and a variety of ketones or aldehydes. This has proved to be the method of choice in the synthesis of complex cyclopentanones via an intramolecular Barbier reaction.[223] Extensions of the use of ultrasound in lithiation reactions have been profitable for a variety of reactions. The Bouveault reaction for the synthesis of aldehydes suffers from side reactions and low yields.

$$\text{R-Li} + (H_3C)_2\text{NCHO} \longrightarrow \text{RCH(OLi)(NCH}_3)_2 \longrightarrow \text{RCHO} \qquad [46]$$

Upon sonication in a cleaning bath, mixtures of organic halides, dimethylformamide, and lithium sand in tetrahydrofuran give very good yields (67-88%) of aldehydes, although no direct comparison to the simple thermal reaction was made.[224] Similar improvements in yields are observed in organocopper conjugate alkylations of enones.[225]



[47]

The formation of the organocopper reagent was accomplished by ultrasonic irradiation of alkyl or aryl bromide solutions in the presence of lithium sand and a solution of a Cu(I) salt; temperature control during the sonication is quite important in these reactions to avoid Barbier-type α-alkylations.

Wurtz-type couplings have also been observed upon sonication of lithium in the presence of both organic halides (yields 36-73%)[226] and chlorosilanes or chlorostannanes (yields 42-94%).[227] Lithium wire is acceptable, but higher

$$R_3M\text{-}Cl + Li \text{ -)-)-)}\rightarrow R_3MMR_3 \quad (M{=}C,Si,Sn;\ R{=}\text{alkyl or aryl}) \qquad [48]$$

yields result with lithium sand dispersed in mineral oil, and requires in some cases a small amount of anthracene as electron transfer catalyst. Direct comparisons to reactions run without ultrasound, but under high speed stirring or heating, were not made.

In the case of dichlorosilanes, oligomerization to form cyclopolysilanes occurs in high yields, with the product's ring size dependent upon the steric bulk of the starting silane.[226] Upon sonication of lithium with the highly hindered bis(mesityl)dichlorosilane, Boudjouk initially reported[228] the synthesis of West's novel disilene[229]:

$$(2,4,6\text{-}(H_3C)_3C_6H_2)_2SiCl_2 + Li \text{ -)-)-)}\rightarrow R_2Si{=}SiR_2 \qquad [49]$$

It is difficult, however, to obtain consistent results with this sonochemical synthesis of the disilene[230], and the generally observed product is the hexamesitylcyclotrisilane.[231]

Ultrasonic irradiation also accelerates the reductive cleavage by Li of phosphorous-carbon bonds in phenyl phosphines.[232,233] Under thermal conditions with vigorous mechanical stirring, the rates are ten times slower in tetrahydrofuran than in the presence of ultrasound provided by a laboratory cleaning bath. The resulting phosphide can then be alkylated with a variety of alkyl halides with yields usually >80%. In the case of α,ω-bis(diphenylposphino)alkanes, themselves synthesized by this route, the process can be repeated to generate various bis(alkylphenylphosphino)alkanes in excellent yields, as shown below. In the absence of ultrasound, this last reaction is very slow with Li and produces significant amounts of side products with K even at -78°C.

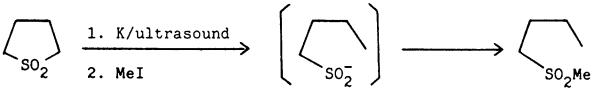
$$Ph_3P + Li \text{ -)-)-)}\rightarrow Ph_2P^{-}Li^{+} \qquad [50]$$

$$Ph_2P^{-}Li^{+} + RX \text{ -)-)-)}\rightarrow Ph_2RP + LiX \qquad [51]$$

$$Ph_2P^{-}Li^{+} + X(CH_2)_nX \text{ -)-)-)}\rightarrow Ph_2P\text{-}(CH_2)_n\text{-}PPh_2 + LiX \qquad [52]$$

$$Ph_2P\text{-}(CH_2)_n\text{-}PPh_2 + Li \text{ -)-)-)}\rightarrow \xrightarrow{RX} PhRP\text{-}(CH_2)_n\text{-}PRPh \qquad [53]$$

The sonochemistry of the other alkali metals is less explored. The use of ultrasound to produce colloidal Na has early origins, and was found to greatly facilitate the production of the radical anion salt of 5,6-benzoquinoline[234] and to give higher yields with greater control in the synthesis of phenylsodium.[235] In addition, the use of an ultrasonic cleaning bath to promote the formation of other aromatic radical anions from chunk Na in undried solvents has been reported.[236] Luche has recently studied the ultrasonic dispersion of potassium in toluene or xylene and its use for the cyclization of α,ω-difunctionalized alkanes, and other reactions[237]. This has been extended to the desulfonylation of cyclic sulfones, which does not occur at useful rates



[54]

in the absence of ultrasound even with a variety of active reductants (including chunk K, K/graphite, Raney Ni, sodium amalgam, or sodium dithionite).[238]

The effects of ultrasound on zinc reagents has been explored in some detail, as well. Ishikawa first examined the use of Zn for trifluoromethylation of carbonyl compounds.[239] In this case the choice of metal was

$$RR'C{=}O + Zn + CF_3I \text{ -)-)-)}\rightarrow RR'(F_3C)COZnI \xrightarrow{H^{+}} RR'C(OH)CF_3 \qquad [55]$$

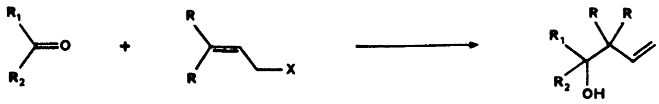
dictated by the relative stability of the perfluoroalkylzinc compounds compared to the corresponding magnesium or lithium species. Good yields (45-86%) were reported for the formation of alcohols from the sonication in a cleaning bath of a mixture of Zn powder and CF_3I in a dimethylformamide solutions of several ketones and aldehydes. The intermediate perfluoroalkylzinc species so formed has also been trapped with CO_2 to give the corresponding perfluoroalkanoic acid in good yields[240].

The closely related Reformatsky reaction has also proven to be assisted by low intensity ultrasound.[241] Extensive comparison to alternative reaction

$$RR'C{=}O + Zn + BrCH_2CO_2R'' \text{ -)-)-)}\rightarrow RR'C(OH)CH_2CO_2R'' \qquad [56]$$

conditions was made in this thorough study. The use of I_2 or I^- promoters and dioxane as solvent is important for optimal yields. Sonication provided reaction rates and yields (typically 30 min. and >90% yield) as good or better than the use of activated zinc powders[242] prepared from the reduction of anhydrous $ZnCl_2$. This work has recently been extended by others to the use of CF_3CHO in the preparation of α-trifluoromethyl-γ-enols[243]. The use of ultrasonically generated organozinc complexes for perfluoroalkylation of allyl, vinyl and aryl halides with Pd(0)[244] catalyst and of alkynes with Cu(0) catalyst[245] has also been reported.

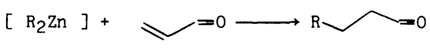
Similarly, allylation of ketones and aldehydes by allylic halides occurs[246] in sonicated aqueous media in the presence of Zn or Sn. The unexpected product is the synthetically useful, rearranged homoallylic alcohol. Although the yields of these reactions are good for both aldehydes and ketones, the relative rates of the aldehydes are much higher: striking selectivity for addition to aldehydic carbonyls in the presence of either intra- or intermolecular ketones is observed.



[57]

Organozinc reagents prepared from ultrasonic irradiation of organic halides with Li in the presence of $ZnBr_2$ have recently been used for conjugate addition to α-enones.[247,248]

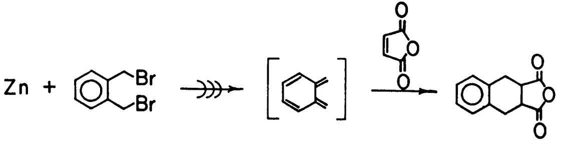
$$R{-}Br + Li + ZnBr_2 \text{ -)-)-)}\rightarrow [\ R_2Zn\ ] \qquad [58]$$



[59]

In the initial report, reactions were run in an ultrasonic cleaning bath cooled with ice, in dry ether or tetrahydrofuran with $Ni(acac)_2$ as catalyst; it was stated that cavitational effects were probably not involved since such solvents supposedly preclude the occurrence of cavitation.[247] In the improved synthesis, however, much more rapid reactions occurred with excellent reproducibility when an immersion horn configuration was used at 0°C with small amounts of tetrahydrofuran dissolved in toluene as solvent.[248] Since the rates are improved by the use of less volatile solvents, this sonochemical reaction probably _is_ due to cavitation. The efficacy of the 1,4-addition is not hampered by β,β-disubstitution of the enone, in contrast to the use of organocopper reagents. This has led to an elegant synthesis of β-cuparenone in three steps and 50% yield.[249] Extension of such conjugate addition of aryl bromides to α,β-unsaturated aldehydes has been made; although the yields are generally ≈60%, it is noteworthy that protection of the starting aldehyde is _not_ necessary.[250]

Low intensity ultrasound has also been applied to the Simmons-Smith cyclopropanation of olefins with diiodomethane reduced by Zn.[251] This reaction normally will not occur without activation of the Zn with, for example, I_2 or Li, and was difficult to scale-up due to delayed initiation. Yields upon sonication of mossy zinc are nearly quantitative, activation of the Zn is unnecessary, and no delayed exotherms are observed. In reactions with another class of organic dihalides, ultrasonic irradiation of Zn with α,α'-dibromo-o-xylene has proved a facile way to generate an o-xylylene-like species, which has been trapped by a variety of dienophiles.[252] This has found synthetic application in the synthesis of functionalized hexahydro-anthracenes and -napthacenes.[253]



[60]

Finally, an improved synthesis of (η^6-1,3,5-cyclooctatriene)-(η^4-1,5-cyclooctadiene)ruthenium(0) has been reported which utilizes a cleaning bath to hasten the Zn reduction of $RuCl_3$ in the presence of 1,5-cyclooctadiene.[254] The use of ultrasound with Zn is a likely area for routine use in the synthesis and reduction of various organometallic complexes.

Two recent reports on the use of ultrasound in organoaluminum chemistry have appeared. The first group prepared a variety of organoaluminum complexes from halocarbons and Al powder[255]; characterization was principally by analysis of organic products after hydrolysis. Yields of subsequent reactions were poor. Of more synthetic interest is the use of ultrasonic irradiation to promote the reaction between ethyl bromide and Al at room temperature; the subsequent reaction of the ethylaluminumsesquibromide ($(CH_3CH_2)_3Al_2Br_3$) so produced with various trialkylborates gave excellent yields of triethylborane.[256]

In all of the heterogeneous organometallic sonochemistry discussed thus far, the metals used have been *extremely reactive* and easily malleable. The specific origin of the rate and yield improvements has not yet been established in these systems. Faster reaction rates come about in part as a consequence of greater surface area dispersions. The improved mass transport between bulk solution and the reagent surface due to cavitational shock waves and microstreaming are also important contributors. These factors permit the use of lower temperatures, with the subsequent advantages of lessened side reactions and improved reaction control. The importance of lattice defects in initiation of the Grignard reaction[257], for example, may be relevant, since surface damage from cavitation is a probable occurrence. Ultrasonic cleaning of the reactive metal surface to remove passivating impurities (e.g. water, hydroxide, metal halide, or organolithium) must also be important.[258] It is interesting to note that heavy use of volatile solvents (especially tetrahydrofuran) has been made. Given the diminution of cavitational intensity under such conditions, future researchers should give thought to less volatile media (*e.g.*, dimethoxyethane, tetrahydrofuran mixed with toluene or decane, bis(2-methoxyethyl)ether (diglyme), etc.); in several cases this has yielded improved results.

4.2.2.3. Transition Metal Reagents

The activation of *less* reactive metals remains an important goal which continues to attract major efforts in heterogeneous catalysis, metal-vapor chemistry, and synthetic organometallic efforts. Given the extreme conditions generated by acoustic cavitation at surfaces, analogies to autoclave conditions or to metal-vapor reactors are not inappropriate. In order to probe the potential generality of ultrasonic activation of heterogeneous reactions, Suslick and Johnson examined[259] the sonochemical reactivity of the normally very unreactive early transition metals with carbon monoxide. Even with the use of "activated", highly dispersed transition metal slurries, as investigated by Rieke,[260,261,262] the formation of the early transition metal carbonyls still require "bomb" conditions (100-300 atm of CO, 100-300°C) and are prepared in only moderate yields.[263] The use of ultrasonic irradiation facilitates the reduction of a variety of transition-metal salts to an active form that will react at low temperatures with low pressures of CO. Reduction of transition metal halides soluble in tetrahydrofuran or diglyme with Na sand using a direct immersion ultrasonic horn under 1-4 atm. CO at 10°C gave fair to good yields of the carbonyl anions for V, Nb, Ta, Cr, Mo, W, Mn, Fe, and Ni.

$$MCl_5 + Na + CO \text{ -)-)-)}\rightarrow M(CO)_6^- \quad (M{=}V,Nb,Ta) \qquad [61]$$

$$MCl_6 + Na + CO \; -)-)-)\!\rightarrow \; M_2(CO)_{10}^{-2} \qquad (M{=}Cr,Mo,W) \qquad [62]$$

Solubility of the metal halide is necessary for effective reaction. An ultrasonic cleaning bath was found to be of only marginal use when compared to the higher intensity immersion horn. Since these reactions are run at low pressures, they may prove uniquely useful in the production of ^{13}CO labeled carbonyl complexes.

The possible mechanisms which one might invoke for the activation of these transition metal slurries include (1) creation of extremely reactive dispersions, (2) improved mass transport between solution and surface, (3) generation of surface hot-spots due to cavitational micro-jets, and (4) direct trapping with CO of reactive metallic species formed during the reduction of the metal halide. The first three mechanisms can be eliminated, since complete reduction of transition metal halides by Na with ultrasonic irradiation under Ar, followed by exposure to CO in the absence or presence of ultrasound, yielded no metal carbonyl.[259] In the case of the reduction of WCl_6, sonication under CO showed the initial formation of tungsten carbonyl halides, followed by conversion of $W(CO)_6$, and finally its further reduction to $W_2(CO)_{10}^{-2}$. Thus, the reduction process appears to be sequential: reactive species formed upon partial reduction are trapped by CO.

Another recent application of ultrasound to the activation of transition metals was reported[221] by Bonnemann, Bogdavovic, and coworkers. An extremely reactive Mg species was used to reduce metal salts in the presence of cyclopentadiene, 1,5-cyclooctadiene, and other ligands to form their metal complexes. The reactive Mg species, characterized as $Mg(THF)_3(anthracene)$, was produced from Mg powder in tetrahydrofuran solutions containing a catalytic amount of anthracene by use of an ultrasonic cleaning bath. A plausible scheme for this reaction has been suggested:

$$Mg + C_{14}H_{10} \; \overset{\text{THF}}{-)-)-)\!\rightarrow} \; Mg(THF)_3(\eta^2\text{-}C_{14}H_{10}) \qquad [63]$$

$$2\ Co(acac)_3 + 3\ Mg(THF)_3(\eta^2\text{-}C_{14}H_{10}) \longrightarrow 2\ Co^* + 3\ Mg^{2+} \qquad [64]$$

$$2Co^* + 2C_5H_6 + 3\ 1{,}5\text{-}C_8H_{12} \longrightarrow 2Co(Cp)(COD) + C_8H_{14} \qquad [65]$$

Table 6

HETEROGENEOUS ORGANOMETALLIC SONOCHEMISTRY

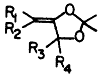
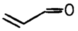
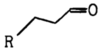
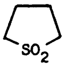
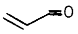
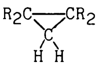
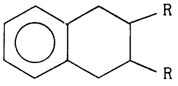
METALLIC REAGENT	ORGANIC REACTANT	PRODUCT	REFERENCES
Hg			
	$(R_2BrC)_2CO$ + $R'CO_2H$	$(HR_2C)CO(C(O_2CR')R_2)$	193,195-198
	$(R_2BrC)_2CO$ + $R'OH$	$(HR_2C)CO(C(OR')R_2)$	199
	$(R_2BrC)_2CO$ + $(H_3C)_2CO$		194
	$C_6H_5(H)(Br)CSC(Br)(H)C_6H_5$	t-$C_6H_5(H)C=C(H)C_6H_5$	200
Mg			
	R-Br	R-MgBr	219,258
	$R_2C=CHCH_2Cl$ + $Mg/C_{14}H_{14}$	$R_2C=CHCH_2MgCl$	220
Li			
	R-Br (R = Pr, n-Bu, Ph)	R-Li	222
	R-Br + R'R"CO	RR'R"COH	222,223
	R-Br + $(H_3C)_2NCHO$	RCHO	227
	R-Br +  + Cu(I)		224
	R_3M-Cl (M=C,Si,Sn; R=alkyl,aryl)	R_3MMR_3	226,227
	R_2SiCl_2 (R=arenes)	cyclo-$(R_2Si)_3$	226,231
Na			
	Arenes	Na(arene$^{-\bullet}$)	234-236
K			
	$XH_2C-(CH_2)_n-CH_2X$	cycloalkanes	237
		$H_3CSO_2C_4H_9$	238

Table 6 (Continued)

METALLIC REAGENT	ORGANIC REACTANT	PRODUCT	REFERENCES
Zn			
	$CF_3I + RR'C=O$	$RR'C(OH)CF_3$	239
	$C_nF_{2n+1}I + CO_2$	$C_nF_{2n+1}CO_2H$	240
	$CF_3I + R\text{-}Br + Pd(0)$	$R\text{-}CF_3$	244
	$CF_3I + RC\equiv CR + Cu(0)$	$HRC=CR(CF_3)$	245
	$RR'C=O + BrCH_2CO_2R''$	$RR'C(OH)CH_2CO_2R''$	241,243
	$PhBr + RCOCH=CHR' + Ni(acac)_2$	$RCOCH_2CHR'Ph$ (R=H, alkyl)	247,248
	$RR'C=O + R''_2C=CHCH_2Br$ (Zn or Sn)	$RR'(HO)CCR''_2CH=CH_2$	246
	$R\text{-}Br + Li + ZnBr_2 +$ 		248,249
	$H_2CI_2 + R_2C=CR_2$		251
	$1,2\text{-}(BrH_2C)_2C_6H_4$ + dienophiles		252,253
	$RuCl_3$ + 1,5-cyclooctadiene	(η^6-1,3,5-cyclooctadiene)-(η^4-1,5-cyclooctadiene)Ru(0)	254
Al			
	$R\text{-}Br + Mg$	AlR_3	219
	CH_3CH_2Br	$(CH_3CH_2)_3Al_2Br_3$	255
	$CH_3CH_2Br + B(OR)_3$	$B(C_2H_5)_3$	256
	$CH_3CH=CHCH_2Br$	$[H_2C=CH(H_3C)C]_3Al_2Br_3$	256
Transition Metals			
	$MCl_5 + Na + CO$ (M=V,Nb,Ta)	$M(CO)_6^-$	259
	$MCl_6 + Na + CO$ (M=Cr,Mo,W)	$M_2(CO)_{10}^{-2}$	259
	$MnCl_3 + Na + CO$	$Mn(CO)_5^-$	259
	$FeCl_3 + Na + CO$	$Fe(CO)_4^{-2} + Fe_2(CO)_8^{-2}$	259
	$NiCl_2 + Na + CO$	$Ni_6(CO)_{12}^{-2}$	259
	$Co(acac)_3 + C_5H_6 + COD + Mg/C_{14}H_{10}$	Co(Cp)(COD)	221

4.2.3. Applications to Heterogeneous Catalysis

Ultrasonic irradiation can alter the reactivity observed during the heterogeneous catalysis of a variety of reactions. Sonication has shown such behavior 1) by altering the formation of heterogeneous catalysts, 2) by perturbing the properties of previously formed catalysts, or 3) by affecting the reactivity during catalysis. There is an extensive (but little recognized) literature in this area,[264] most of which is beyond the scope of this review.

In general, however, ultrasonic rate enhancements of heterogeneous catalysis are usually relatively modest (less than tenfold). The effect of irradiating operating catalysts is often simply due to improved mass transport.[265] In addition, increased dispersion during the formation of catalysts under ultrasound[266] (e.g., Ziegler-Natta polymerizations[267]) will enhance reactivity, as will the fracture of friable solids (e.g., noble metals on C or silica[182] or malleable metals[268]). In the case of bulk metal catalysts, the removal of passivating coatings through surface cavitational damage is well established.[269,270,271]

The range of reactions which have been examined is wide[264] and includes hydrogenations[272], ammonia synthesis[273], polymerizations[267], and oxidations.[274] Little activity has occurred in this area during the past few years. Recent reports of the effects of sonication on heterogeneous catalysis include the liquefaction of coal by hydrogenation with Cu/Zn,[275] the hydrogenation of olefins by formic acid with Pd on carbon,[276] the hydrogenation of benzyl ethers by 1 atmosphere of H_2 with Pd on carbon,[277] and the hydrosilation of 1-alkenes by Pt on carbon.[278]

5. CONCLUDING REMARKS

The use of ultrasound in both homogeneous and heterogeneous reactions was essentially nil five years ago. Its application in a variety of reactions, especially heterogeneous reactions of highly reactive metals, is now becoming commonplace. The sonochemical generation of organometallic species as synthetic intermediates will continue to find application in nearly any case where interphase mixing is a problem. Much less explored, but potentially quite exciting, is the use of sonochemistry to create high-energy chemistry in condensed phases at room temperature. Unique examples of sonochemical reactivity quite different from thermal or photochemical processes have been noted. The analogies to shock-wave and gas-phase pyrolyses, to "bomb" reactions, and to metal vapor chemistry will prove useful guides in this exploration.

A primary limitation of sonochemistry in homogeneous media remains its energy inefficiency. This may be dramatically improved, however, if a more efficient means of coupling the sound field with preformed cavities can be found. The question of selectivity in and control of sonochemical reactions, as with any thermal process, remains a legitimate concern. There are, however, clearly defined means of controlling the conditions generated during cavitational collapse, which permit the variation of product distributions in a rational fashion.

6. REPRESENTATIVE EXPERIMENTAL PROCEDURES

The experimental factors which influence sonochemical reactions have already been discussed in some detail. For purposes of illustration, the experimental procedures of several of the more useful synthetic reactions have been taken from the literature essentially without modification and are presented below. Their order follows the sequence used in the text.

6.1. Reduction of Aryl Halides with Lithium Aluminum Hydride[208]

10 mmol of o-bromotoluene and 10 mmol of $LiAlH_4$ were added to 10 mL of dry dimethoxyethane. The reaction mixture, contained in a 100 mL round bottom single neck flask and maintained under a N_2 atmosphere, was partly submerged in a laboratory ultrasonic cleaner at 35°C. Cavitation produced a turbid reaction mixture immediately and after 5h the reaction was quenched and the products isolated. The product mixture was first poured slowly onto an ice-CH_2Cl_2 slurry with stirring. This was extracted twice with CH_2Cl_2 and the extracts were dried over $MgSO_4$. Solvent was removed by distillation. Isolated yield was 98%.

6.2. Preparation of Dichlorocyclopropanes[201]

A mixture of powdered NaOH (20 mmol) and styrene (2 mmol) dissolved in 20 mL of chloroform was placed in a 100 mL, three-necked, round- bottomed flask equipped with a mechanical stirrer. The flask was immersed in an ultrasonic cleaning bath and was positioned approximately 1 cm above the floor of the cleaning bath. The mixture was then simultaneously stirred and irradiated with ultrasound for 1.5 h. The temperature of the bath never exceeded 40°C. The contents were then centrifuged and the organic layer separated. After chloroform was removed under reduced pressure, the residue was dissolved in ether, washed with water, dried ($MgSO_4$), and distilled (Kugelrohr) to give 95% yield of 1,1-dichloro-2-phenylcyclopropane.

6.3. Synthesis of Thioamides[207]

2.0 mmol of N-methylacetanilide was dissolved in anhydrous tetrahydrofuran (20 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was placed in an ultrasonic cleaning bath which contained a submerged, air-driven magnetic stirrer. To the reaction solution was added P_4S_{10} (1.0 mmol), the magnetic stirrer was started, and the reaction mixture was irradiated for 20-30 min. Within the first 15 min. a nearly homogeneous solution was obtained, followed shortly by the formation of a white, phosphorous-containing precipitate. An addition portion of P_4S_{10} (1 mmol) was added to the mixture and sonication with efficient stirring was continued for an additional 30 to 90 min. The final bath temperature never exceeded 40°C. The heterogeneous mixture was cooled to ambient temperature and filtered. The solid byproduct was washed with several small portions of CH_2Cl_2, the filtrates were combined, and solvents removed in vacuo, giving a residue which was purified by flash chromatography on silica gel. A 97% yield of N-methylthioacetanilide was so obtained.

6.4. Reductive Acyloxylation of α,α'-Dibromo Ketones[197]

2 g. of 2,4-dibromo-2,5-dimethyl-3-hexanone was added to a 25 mL Erlenmeyer flask, together with 15 mL of acetic acid. A 7 mL amount of mercury was added to the flask, which was then sealed with a rubber serum cap and placed in an ultrasonic cleaning bath maintained at 14°C for 72 h. At the end of this time, the flask was allowed to stand for some time to permit suspended solids to settle. The clear supernatant liquid was removed, and the mercury-solid sludge was washed with CCl_4 by decantation. The combined organic extracts were washed with water, saturated $NaHCO_3$, and water and dried over $MgSO_4$. The solvent was removed at the rotary evaporator to afford the crude 2-acetoxy-2,5-dimethyl-3-hexanone in 89% yield.

6.5. Formation and Reaction of Organocopper Reagents with Enones[225]

1-Bromobutane, lithium sand (suspension in mineral oil), CuI (1.5 mmol each) and 2-cyclohexenone (1.0 mmol) at 0°C in diethyl ether-tetrahydrofuran (1:1) under an Ar atmosphere were sonicated in a thermostated ultrasonic cleaning bath. The metallic lithium was rapidly consumed (3-5 min), after which the resultant black mixture was poured into saturated aqueous NH_4Cl. Ether was added and the organic layer washed and dried. Evaporation and purification by silica gel chromatography afforded 89% yield of the β-alkylated ketone.

6.6. Trifluoromethylation of Carbonyl Compounds with CF_3I and Zn[239]

A flask containing commercially available Zn powder (20 mmol), trifluoromethyl iodide (11 mmol), and benzaldehyde (10 mmol) in N,N-dimethylformamide (25 mL) was irradiated in an ultrasonic cleaning bath for 30 min. Then, the solution was poured into a 2% HCl solution and an oily material was extracted with diethyl ether. After the ethereal solution was dried over $MgSO_4$, the solvent was removed. Distillation gave phenyltrifluoromethylcarbinol in a yield of 72%.

6.7. Reformatsky Reaction[241]

An oven-dried, N_2 filled, 250 mL, single necked, round-bottomed flask was charged with 25 mL of dioxane, 75 mmol butanal, 90 mmol of ethyl bromoacetate, and 130 mmol of Zn dust. The flask was immersed to the solvent level in an ultrasonic cleaner, and I_2 was added to the slurry until it became exothermic. This required about 2 mmol of I_2. After about 5 minutes, the product mixture was poured into an ether-ice slurry with stirring, and 1 g of KI was added to remove I_2 from the organic layer. This was extracted with ether and the combined extracts dried over $CaCl_2$. Removal of the volatiles by flash evaporation followed by vacuum distillation gave 91% yield of ethyl-3-hydroxyhexanoate.

6.8. Activation of Early Transition Metals[259]

Sonication was carried out with a high intensity immersion ultrasonic horn in a sealed atmosphere reaction cell. 1 mmol of $MoCl_5$ was dissolved in 30 mL of tetrahydrofuran and 1.2 mmol of Na sand was added. The mixture was flushed with CO and maintained under CO during sonication. The system was thermostated so that the maximum temperature reached during the reaction was 10°C; sonications were carried out for 17 h. The reaction mixture was filtered under N_2 and the solvent removed in vacuo. Yields of $Na_2Mo_2(CO)_{10}$ were 54% when run under 4.4 atmospheres of CO and 39% when under 1 atmosphere.

6.9. Activated Mg in the Synthesis of Transition Metal Complexes[221]

Magnesium powder (300 mmol; particle size <0.1 mm) was treated under Ar with 6.2 mmol anthracene, 300 mL tetrahydrofuran (purified over $NaAl(C_2H_5)_4/LiAlH_4$) and 0.1 mL CH_3I. On stirring at 23°C a yellow-green solution was formed, from which orange colored anthracene-magnesium separated in ca. 1-2 h. The mixture was subjected to an ultrasonic cleaning bath for 3 h and heated with stirring to 65°C. After addition of 250 mmol cyclooctadiene and 111 mmol monomeric cyclopentadiene, the source of heat was removed and solid cobalt(III) acetylacetonate (100 mmol) added portionwise to the continually stirred solution over 15 min, whereby the solution vigorously boiled. After cooling to 20°C and filtration, the clear filtrate was evaporated to dryness in a high vacuum. The residue was taken up in 500 mL pentane and the solution filtered again through an ultrafine frit. The complex cyclooctadienyl-cyclopentadienylcobalt crystallized from the clear solution at -80°C; yield 79%.

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