

Organometallic Sonochemistry

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I

INTRODUCTION AND INTENT

In 1894, the destroyer H.M.S. Daring failed to meet specifications: its speed and efficiency were inexplicably low. Sir John Thornycroft and Sidney Barnaby observed severe vibration and excessive slippage of the ship's screw propeller. After replacing four sets of blades, a solution to the problem was found by simply increasing the surface area of the propeller and decreasing its angular velocity. Their description of the observation of associated bubble formation on the moving propeller was the first report of the phenomenon known as cavitation (1), which occurs both during turbulent flow and during ultrasonic irradiation of liquids. In attempting to explain such observations, Lord Rayleigh described (2) in 1917 the first mathematical model for the collapse of cavities in incompressible liquids and predicted *enormous* local temperatures (10,000 K) and pressures (10,000 atm) during such collapse.

The chemical (3) and biological (4) 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

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 "nonlinear" 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 waves' displacement amplitude. An extensive literature dealing with nonlinear propagation of sound exists (9,13,14), 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: we therefore will consider separately cavitation in a homogeneous liquid and cavitation near a liquid–solid interface.

A. Nucleation of 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 (15). 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 submicrometer filtering, water will withstand only -200 atmospheres for a few seconds (16). One also needs to rationalize two other methods which increase the cavitation threshold: vacuum degassing (17) and initial hydrostatic pressurization (18). 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 micrometers in radius) will redissolve in a few seconds, whereas larger ones will rapidly rise to the surface (19). The nucleation mechanism generally accepted at this time involves gas entrapped in small-angle crevices of particulate contaminants (20–22) as shown schematically in Fig. 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

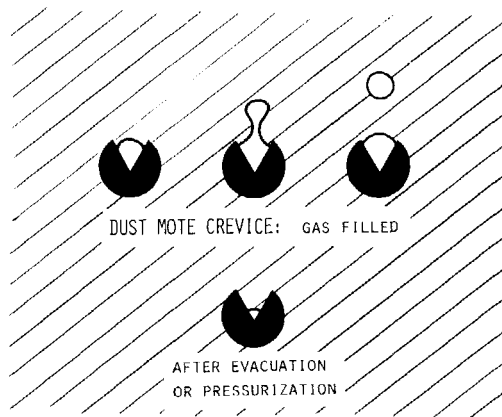


FIG. 1. Nucleation of acoustic cavitation.

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 (23).

B. Cavitation in Homogeneous Media

Flynn proposed the generally accepted division of cavitation phenomenon 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 (24). 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 transient cavitation which gives rise to sonochemistry. An idealized pictorial representation of this scheme is shown in Fig. 2. Several exhaustive reviews of acoustic cavitation dynamics have been published (8,25-27) so this discussion will be limited to a qualitative overview.

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 nonideal liquid properties (28-33). Let us examine, as an example, one such equation of

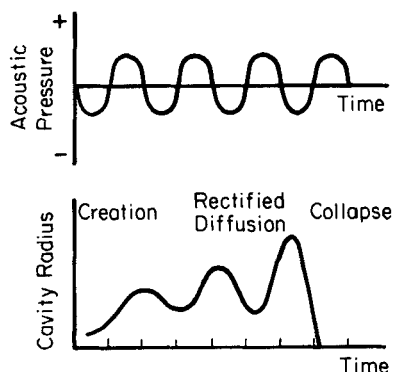


FIG. 2. Idealized representation of Bubble growth and collapse during transient cavitation.

motion, developed by Plesset (28):

$$\rho R \ddot{R} + 1.5(\rho \dot{R}^2) - (P_0 + 2\sigma/R_0)(R_0/R)^{3\gamma} + P_0[1 - (P_A/P_0) \cos(\omega t)] + 2\sigma/R + 4\mu \dot{R}/R = 0 \quad (1)$$

where R is the instantaneous radius of the cavity, \dot{R} and \ddot{R} the velocity and acceleration, respectively, of the bubble's surface, R_0 the equilibrium radius, P_0 the ambient pressure, P_A the acoustic pressure amplitude, $P_0 + 2\sigma/R_0$ the effective pressure inside the cavity at the equilibrium radius, ω the acoustic frequency, ρ the liquid density, σ the surface tension, μ the effective liquid viscosity, and γ the polytropic exponent of the gas within the bubble. The inertial effects are contained in the first two terms, the internal pressure in the third, the external applied pressure in the fourth, the surface tension in the fifth, and viscosity damping in the sixth. Such equations have been solved numerically for varying degrees of approximation. All have difficulty, however, in accurately calculating the dynamics of bubble motion during the latter stages of implosive collapse where sonochemical events are expected to originate.

One can easily calculate from such equations, however, what size cavity would undergo maximum expansion when subjected to a given acoustic field. Minnaert, for example, derives (34) (from a simplified model which assumed a noncondensable gas and neglected viscosity) this resonant size of a transient cavity as

$$R_r = (2\pi\omega)^{-1} (3\eta P_0/\rho)^{1/2} \quad (2)$$

where R_r is the resonant size. More complete determinations (8) do not lead to significant differences for frequencies less than 300 KHz at $P_0 = 1$

atmosphere. At 20 KHz, a typical frequency of laboratory ultrasonic irradiations, R_r is calculated to be $170 \mu\text{m}$ and at 1 MHz, $3.3 \mu\text{m}$.

Bubbles which are well below this optimal resonant 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. The first class involves Blake's mechanism for transient cavitation, in which the bubble grows rapidly under the instigation of the expansion wave of a single acoustic cycle (35-38). The minimum acoustic pressure at which such growth can still occur (the "Blake threshold") is derived from equations of motion similar to the one already discussed, in terms of the ambient pressure, the liquid surface tension, and the initial radius of the bubble. Bubbles much larger than this resonant size will not be capable of undergoing transient cavitation due to the nonnegligible inertial term: they would be unable to respond to the imposed pressure changes within the time frame of the acoustic frequency.

Cavities below this resonant size are still capable of growth, however, through the process known as rectified diffusion (39,40). 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-

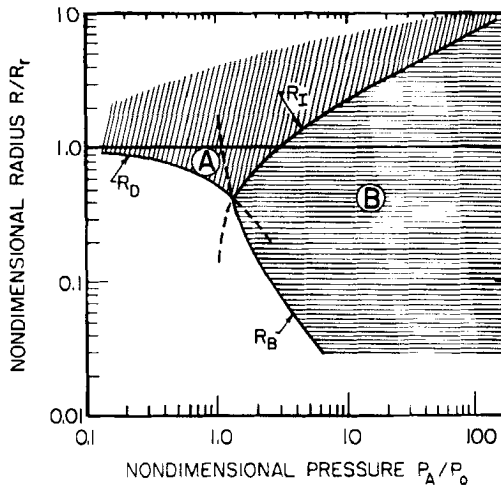


FIG. 3. Thresholds of cavitation. Region A: Bubble growth through rectified diffusion only. Region B: Bubble growth through transient cavitation. R_D , Threshold for rectified diffusion; R_I , threshold for predomination of inertial effects; R_B , Blake threshold for transient cavitation. [After R. E. Apfel (8).]

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. Since rectified diffusion will increase the size of cavities below the Blake threshold, it represents the "stable cavitation" threshold. Free standing bubbles below this size will not grow during ultrasonic irradiation and will therefore rapidly redissolve. These results can be graphically represented in Fig. 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/second) of laser generated cavitation (41). As seen in Fig. 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.

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 (42,43) and electrical discharge (44,45). The implosive collapse of a bubble will obviously 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 (46,47)] have not been well-developed on a molecular level and recently have been thoroughly rebutted as inconsistent with observed sonochemical reactivities and sonoluminescent behavior (48,49). 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 ($\sim 10^5 g$ at 500 KHz) (50). Secondary reactions with high energy species produced from solvent sonolysis also contributes to polymer degradation. Finally, generally small rate enhancements (51-53) [$<20\%$, although there is one report of a 10-fold increase (54)] of solvolysis reactions have been reported and have been interpreted in terms of a disruption of the solvent structure (55) by the ultrasonic irradiation. The details of this proposed mechanism remain undiscussed.

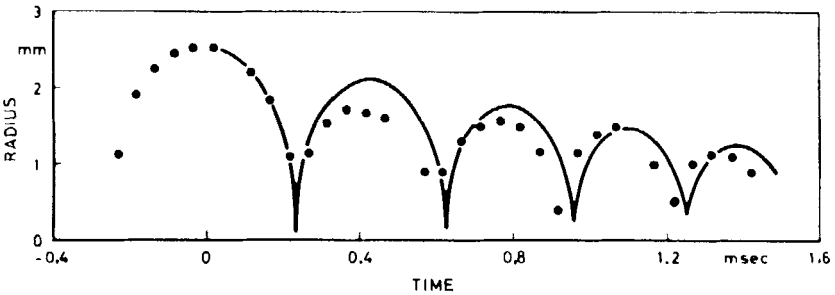
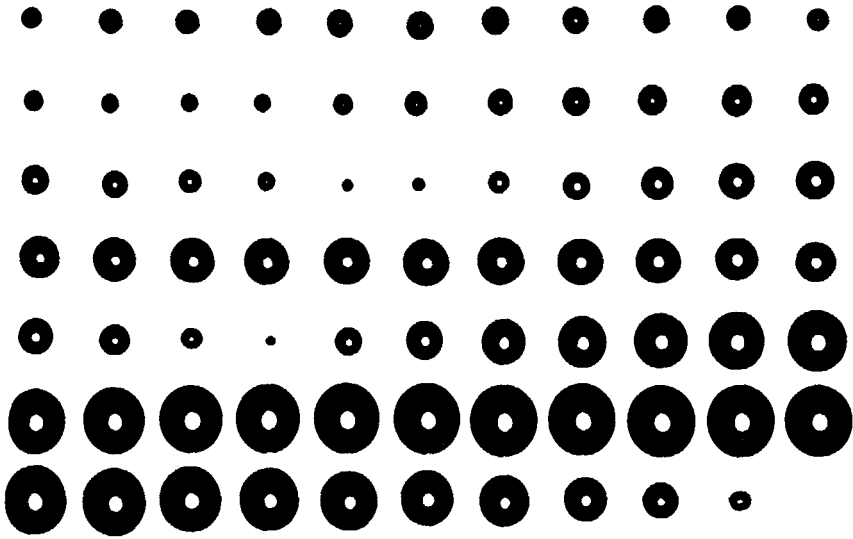


FIG. 4. Dynamics of bubble motion. Laser-induced cavitation in silicone oil: upper portion is the experimental observations at 75,000 frames/second; lower curve compares the experimentally observed radius versus theory. [W. Lauterborn (41).]

The high temperatures and pressures created during transient cavitation are difficult both to calculate and to determine experimentally. The simplest models of collapse, which neglect heat transport and the effects of condensable vapor, predict maximum temperatures and pressures as high as 10,000 K and 10,000 atmospheres. More realistic estimates from increasingly sophisticated hydrodynamic models yield estimates of ~ 5000 K and ~ 1000 atmospheres with effective residence times of < 100 nseconds, but the models are very sensitive to initial assumptions of the boundary conditions (30–32).

There are only four experimental determinations of cavitation conditions. The first involves spectral analysis of sonoluminescent emission (56), for example, of excited state Na atoms generated upon sonolysis of aqueous NaCl 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, however, it seems that 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 (57). The second probe of cavitation conditions, which also relied on sonoluminescence data, utilized the relative emissivity of NO- and NO₂-saturated water and estimated temperatures of ~1000 K in aqueous solutions at 285 K bulk temperature irradiated at 459 MHz (58). A recent analysis (59) of aqueous sonoluminescence in terms of blackbody radiation gives estimates of ~5500 K; since such sonoluminescence had previously been conclusively demonstrated to derive from chemiluminescence of radical recombinations (60), this approach appears without validity. The last experimental determination of cavitation conditions utilizes the comparative-rate, "chemical thermometry" approach, originally used (61) in shock tube experiments. In this work the relative rates of CO dissociation of metal carbonyls were determined as a function of substrate vapor pressure (62,63) 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 Fig. 5; the ratio of the volumes of the gas to liquid reaction zones was ~10⁵. The effective temperatures were determined to be 5200 K for the gas-phase site and ~1900 K for the liquid shell for alkane solvents sonicated under 1 atm Ar at 20 KHz with an overall vapor pressure of 5.0 torr. Given the differences in irradiation

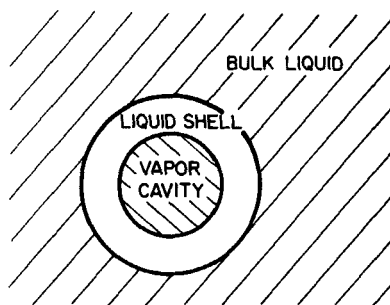


FIG. 5. The two-site model of sonochemical reaction zones.

conditions 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 cavitation collapse is producing hot-spots with effective temperatures of several thousand degrees.

C. Cavitation at Surfaces

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 spherical implosion of the cavity occur, but instead a markedly asymmetric collapse happens which generates a jet of liquid directed at the surface, as seen in the high speed microphotographs taken by Ellis (64,65) and Lauterborn (66) and shown in Fig. 6. The tip jet velocities measured by Lauterborn are greater than 100 m/second. 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 (67) as shown in

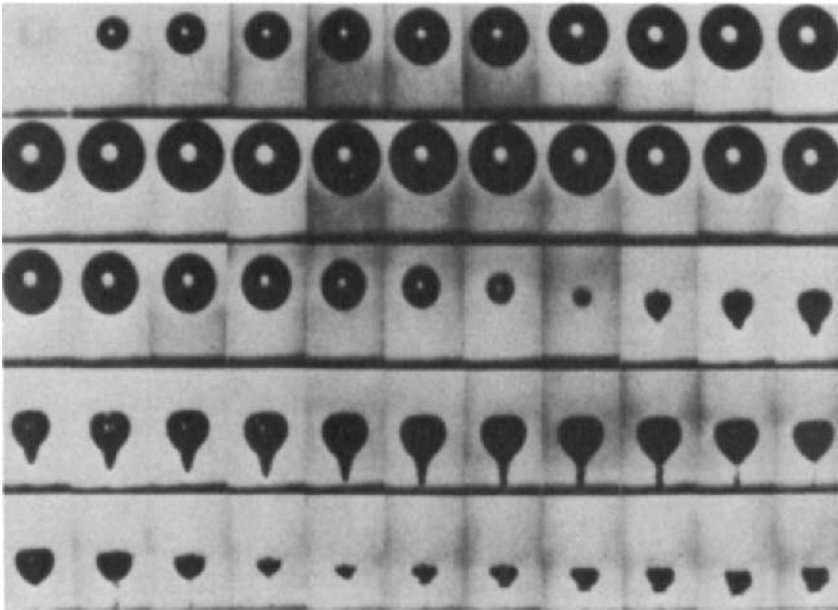


FIG. 6. Cavitation near a surface. Jet formation from laser-induced cavitation in water at 75,000 frames/second. Sequence is from left to right, top to bottom; the solid boundary is at the bottom of each frame. From Ref. 66.

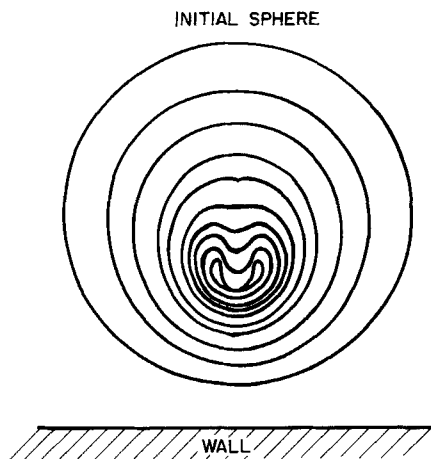


FIG. 7. Theoretical surface profiles of collapsing bubble near a boundary. Initially, the distance of the bubble's edge from the boundary was $R_0/2$. [After E. A. Neppiras (26).]

Fig. 7. The impingement of this jet can create a localized erosion (and even melting) responsible for surface pitting and ultrasonic cleaning (68–70). A second contribution to erosion created by cavitation involves the impact of shock waves generated by cavitation collapse. The magnitude of such shock waves can be as high as 10^4 atmospheres, which will easily produce plastic deformation of malleable metals (71). The relative magnitudes of these two effects depends heavily on the specific system under consideration.

Acoustic streaming is another nonlinear acoustic phenomenon important to the effect of ultrasound on surfaces (9,72). 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. Such streaming will occur at moving solid surfaces or at vibrating bubbles. Thus, when a liquid–solid interface is exposed to ultrasound, improved mass transport is expected owing to acoustic streaming. This will occur even when the sound field is a stable standing wave in the absence of cavitation (73).

Enhanced chemical reactivity of solid surfaces are associated with these processes. The cavitation 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.

The effect of ultrasound on liquid-liquid interfaces between immiscible fluids is emulsification. This is one of the major industrial uses of ultrasound (74-76) and a variety of apparatus have been devised which will generate micrometer-sized emulsions (9). The mechanism of ultrasonic emulsification lies in the shearing stresses and deformations created by the sound field of larger droplets. When these stresses become greater than the interfacial surface tension, the droplet will burst (77,78). 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.

III

EXPERIMENTAL INFLUENCES ON SONOCHEMISTRY

A. 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 voltage, alternating current with an ultrasonic frequency (roughly 15 KHz to 1 MHz). 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 means of control of the acoustic intensity, which will vary from bath to bath and over the lifetime of a single cleaning bath. In addition, their acoustic frequencies are not well controlled and differ from one manufacturer to another, and 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 (79). Similarly, the height of the bath liquid and of the solution within the reaction vessel are extremely important (79,80). Temperature control is often neglected with this apparatus. Since the bath temperature can rise >25 K during the course of a long irradiation, this can significantly influence both the intensity of the cavitation 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 Fig. 8, was originally designed for cell disruption but has been adopted for sonochemical studies as well (81). It has greater acoustic intensities, better frequency control, and potentially better thermostating than the cleaning bath. Again, however, it 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.

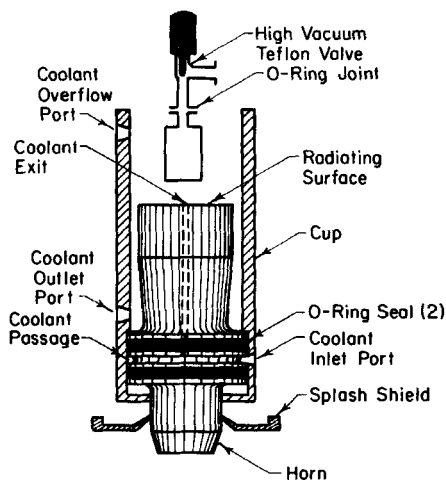


FIG. 8. Cup-horn sonicator. Modification of a design from Heat Systems-Ultrasonics, Inc. (81,82).

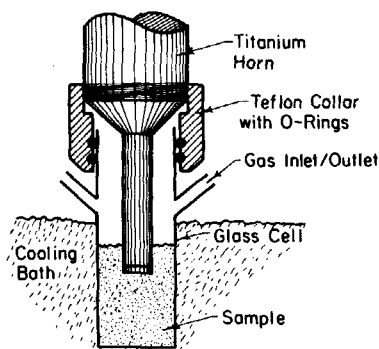


FIG. 9. Direct immersion ultrasonic horn equipped for inert atmosphere work. [Design of K. S. Suslick (183).]

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.

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 Fig. 9, or for moderate pressures (<10 atmospheres). These devices are available from several manufacturers (82) at modest cost and are used primarily for cell disruption. A variety of sizes of power supplies and titanium horns are available, thus allowing flexibility in sample size. 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.

A rough, but useful, comparison between typical sonochemical and photochemical efficiencies is shown in Table I. 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

TABLE I
COMPARISONS BETWEEN SONOCHEMICAL AND PHOTOCHEMICAL APPARATUS

	Photochemistry	Homogeneous sonochemistry	Heterogeneous sonochemistry
Source	250 W Quartz-Halogen	200 W Cell disrupter (at 60% power)	150 W Cleaning Bath
Approximate cost (1985)	\$1800	\$1900	\$700
Typical rates	7 $\mu\text{mol}/\text{minute}$	10 $\mu\text{mol}/\text{minute}$	500 $\mu\text{mol}/\text{minute}$
Electrical efficiency	2 mmol/kWh	5 mmol/kWh	200 mmol/kWh

energy inefficiency due to the 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 irradiation is extant technology. Liquid processing rates of 200 liters/minute are routinely accessible from a variety of modular, in-line designs with acoustic power of several kW per unit (83). 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 (74). While these units are of limited use for most laboratory research, they are of potential importance in eventual industrial application of sonochemical reactions.

B. Extrinsic Variables

Sonochemistry is strongly affected by a variety of external parameters, including acoustic frequency, acoustic intensity, bulk temperature, static pressure, choice of ambient gas, and choice of solvent. These are important considerations in the effective use of ultrasound to influence chemical reactivity, and are also easily understandable in terms of the cavitation hot-spot mechanism. A summary of these effects is given in Table II.

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 hertz to a few megahertz (26)]; observed sonochemical rates may change, but controlled comparisons of efficiency are lacking at this time and will prove difficult to obtain.

TABLE II
THE EFFECTS OF EXTRINSIC VARIABLES OF SONOCHEMISTRY

Extrinsic variable	Physical property	Effect
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
Choice of liquid	Gas solubility	Bubble content
	Vapor pressure	Intensity of collapse
	Surface tension	Transient cavitation threshold
	Viscosity	Transient cavitation threshold
	Chemical reactivity	Primary or secondary sonochemistry

For example, the observed sonochemistry of aqueous solutions is unchanged over this entire range (84). At very high frequencies (above a few megahertz), cavitation ceases, and sonochemistry is generally not observed (85,86). The observed thresholds for cavitation in homogeneous liquids are strongly frequency dependent (8); 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 size of the zone of liquid undergoing cavitation, 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 Fig. 3); this too will increase the observed sonochemical rate. It is often observed experimentally, however, that as one continues to increase acoustic amplitude, rates eventually begin to diminish again (87). 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 may occur (88).

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 (89). From simple hydrodynamic models of the cavitation process, Neppiras, for example, derives (26) the peak temperature generated during collapse of a gas-filled cavity as

$$T_{\max} = T_0 P_a (\gamma - 1) / Q \quad (3)$$

where T_0 is the ambient temperature, P_a the acoustic pressure just prior to collapse, γ the polytropic ratio (the ratio of specific heats, C_p/C_v), and Q the gas pressure in the bubble prior to collapse. In the case of vapor-filled cavities, we may take Q to be roughly approximated by P_v , the vapor pressure of the system, and the maximum temperature of the collapse will be inversely proportional to the vapor pressure of the system. Assuming Arrhenius behavior ($\ln k = \ln A - E_a/RT_{\max}$), one expects that the sonochemical rate coefficient should follow

$$\ln k = \ln A - \{E_a/[RT_0 P_a (\gamma - 1)]\} P_v \quad (4)$$

This is only a rough approximation since it neglects the effects of both thermal conductivity and vapor condensation during collapse. Nonetheless, the linear correlation of $\ln k_{\text{obs}}$ and P_v is the experimentally observed behavior in a wide range of sonochemical systems in a variety of solvents (89,90). It has also been suggested that the effect of ambient temperature lies in the change in ambient gas solubility (6), although a plausible mechanism for such an influence was unstated. Recent results in which temperature, solvent vapor pressure, and gas solubility have been varied independently (89,90) rule out gas solubility as an important variable. When secondary reactions are being observed (as in secondary corrosion or other thermal chemical reactions occurring after initial acoustic erosion of a passivated surface), then temperature can play its usual role in thermally activated chemical reactions. This explains the occasional observation of increasing rates of corrosion associated with cavitation with increasing temperature (91).

Sonochemical yields as a function of increasing static pressure have been reported by different researchers to increase (6), to decrease (92), and to increase to some point and then decrease (93). One would expect that cavitation 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 one reduces the ambient pressure, eventually one will deactivate the gas-filled crevices which serve as nucleation sites (discussed earlier) and therefore also diminish observed sonochemistry. 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 experimental results are conflicting on this question. 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. As shown in Eq. (3), 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 the difference between cavitation in the presence of xenon ($\gamma = 1.67$) and a freon ($\gamma \approx 1.1$), for example, would yield a ratio of maximum temperatures of sevenfold! Sonochemical rates are also significantly influenced by the ambient gas's thermal conductivity, as shown in Fig. 10, so even the noble gases affect cavitation differently (94,95). The role of thermal transport during cavitation collapse has been long recognized as evidence in favor of the hot-spot mechanism of sonochemistry (94), and recent calculations underscore its effect on conditions generated during cavitation collapse (30,31). In addition, sonochemical reactions will often involve the gases present in the cavitation event (96). 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, as discussed later. Another relevant parameter, gas solubility, has been observed to affect the concentration of cavitation nuclei (97) and, in this way, it may play a role in determining the observed cavitation threshold.

The choice of the solvent has a profound influence over the observed sonochemistry as well. The effect of vapor pressure has already been mentioned. Other liquid properties, such as surface tension and viscosity, will alter the threshold of cavitation (8), 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 $OH\cdot$ and $H\cdot$ 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 (89). One may minimize this

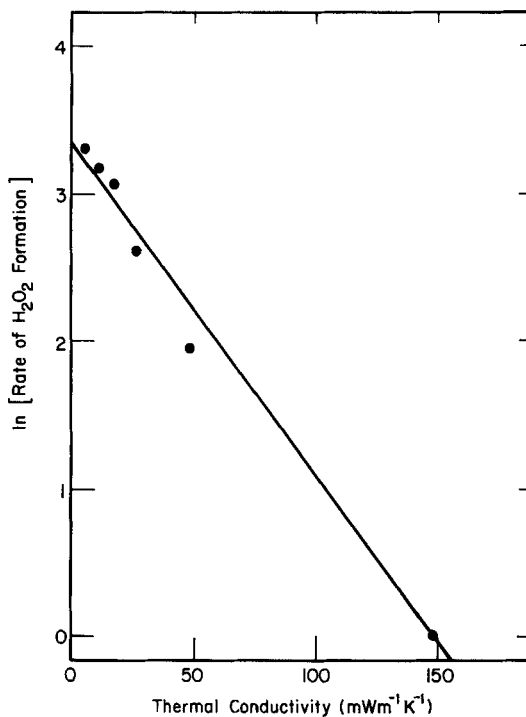


FIG. 10. Sonochemical rates as a function of ambient gas thermal conductivity. [Replotted data from R. O. Prudhomme (95).]

problem, however, by using robust solvents (avoiding halocarbons, in particular) which have low vapor pressures in order to reduce their concentration in the vapor phase of the cavitation event. Furthermore, under the conditions used for heterogeneous sonochemistry, cavitation is primarily at the surface and dominates the observed reactivity. Similarly, one must anticipate secondary solvent reactivity in the trapping of high energy species produced during cavitation.

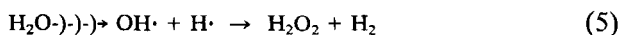
Thus, the parameters of acoustic intensity, temperature, ambient gas, and solvent choice have strong influences on sonochemical reactions. It is clear that one can fine tune the energetics of cavitation by the use of these variables and hence exercise control on the rates and reaction pathways followed 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 provides easy mechanisms for experimental control of the peak temperatures generated during the cavitation collapse.

IV

OVERVIEW OF THE CHEMICAL EFFECTS OF ULTRASOUND

A. Aqueous Sonochemistry

The early studies of the chemical effects of ultrasound have been thoroughly reviewed (5-7). Only the most important and most recent research is mentioned here as needed to provide a perspective on sonochemical reactivity patterns. The sonolysis of water is the earliest and most *exhaustively* studied (3,93,96,98-105). The first observations on the experimental parameters which influence sonochemistry come from these reports. The primary products are H₂O₂ and H₂, and various data supported their formation from the intermediacy of hydroxyl radicals and hydrogen radicals:



Spin trapping experiments (106) have recently provided the final definitive evidence for the intermediacy of OH· and H·, but data have also suggested the formation of a variety of other high energy species, depending on conditions (ambient gas, pH, etc.), including $e^-_{(\text{aq})}$ (107) and HO₂· (108). In the presence of O₂, isotope labeling studies show that much of the peroxide derives from the O₂, without O—O bond cleavage, rather than directly from the water. This clearly must involve a redox process of O₂, for example, with H·. Under typical laboratory sonolysis with an immersion horn, the rate of formation of peroxide will be ~30 μM/minute.

Given the facile homolytic cleavage of water during ultrasonic irradiation, a wide range of secondary sonochemistry in aqueous solutions would be expected and indeed has been repeatedly observed. Cited in Table III are those aqueous sonochemical reactions in which products have been well characterized; in some cases, trace amounts of other products were reported in addition to the major products listed. An extensive list of oxidations and reductions have been reported of various inorganic species. Various organics have been sonicated either as aqueous solutions or suspensions, generally with a wide range of highly degraded products being formed. Since extremely reactive intermediates are formed at respectable rates from the sonolysis of water itself, it is not surprising to see this general lack of control of 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.*

TABLE III
AQUEOUS SONOCHEMISTRY

Substrate present	Principal products	Ref.
<i>Gases</i>		
O ₂	H ₂ O ₂ , O ₃	102,103
N ₂	HNO ₂ , HNO ₃ , NH ₂ OH, NH ₃	96,109
N ₂ + H ₂	NH ₃	110
CO + H ₂	HCHO	109
N ₂ + (CO, CH ₄ , or HCHO)	Amino acids	109,111
<i>Inorganics</i>		
Br ⁻ , Cl ⁻	Br ₂ , Cl ₂	112
Ce ⁴⁺	Ce ³⁺	113
Co(NH ₃)N ₃ ²⁺	Co ²⁺ + N ₃	114
Fe ²⁺	Fe ³⁺	115,116
Fe(III)(C ₂ O ₄) ₃ ³⁻	Fe ²⁺	117
H ₂ S	H ₂ + S ₈	118
I ⁻	I ₃ ⁻	81,85,100
MnO ₄ ⁻	MnO ₂	119
NO ₃ ⁻	NO ₂ ⁻	120
OsO ₄	OsO ₂	121
PO ₃ ²⁻	PO ₄ ²⁻	122
Tl ⁺	Tl ³⁺	123
<i>Organics</i>		
CCl ₄	Cl ₂ , CO ₂ , HCl, C ₂ Cl ₆ , HOCl	42,100,124-126
CH ₃ I	CH ₄ , I ₂ , CH ₃ OH, HI, C ₂ H ₆	127
R ₂ CHCl	R ₂ CHOH, HCl	52-54
Cl ₃ CCH(OH) ₂	HCl	128,129
C ₆ H ₅ Br	Br ⁻ , C ₂ H ₂	130,131
Maleic acid + Br ₂	Fumaric acid	132,133
CS ₂	S ₈ , H ₂ S	134
(C ₄ H ₉) ₂ S	(C ₄ H ₉) ₂ SO, polymer	135
RCHO	CO, CH ₄ , C ₂ H ₄ , C ₂ H ₄ O ₂ , RCO ₂ H	136
HCO ₂ ⁻	CO ₂	137
C ₅ H ₅ N	HCN, C ₂ H ₂ , C ₄ H ₂	131,138
C ₆ H ₅ OH	C ₆ H ₄ (OH) ₂	139
C ₆ H ₅ CO ₂ H	C ₆ H ₄ (OH)(CO ₂ H)	140
C ₆ H ₁₁ OH	C ₂ H ₂	141
RCO ₂ H	CO, CH ₄	136
RCO ₂ R'	RCO ₂ H, R'OH	51,142-146
RCH ₂ NH ₃	H ₂ , CH ₄ , NH ₃ , RCHO, RCH ₂ OH	147
(CH ₂ NH ₂) ₂	NH ₃	123
Thymine	Hydroxylated products	7,148,149
Uracil	Hydroxylated products	7,150,151
Various amino acids	H ₂ , CO, NH ₃ , RNH ₂ , HCHO	152
Cysteine	Cystine	152
<i>Macromolecules</i>		
C ₆ H ₅ CHCH ₂	Polymerization	153
H ₂ CC(CH ₃)(CO ₂ H)	Polymerization	154
H ₂ CCH(CONH ₂)	Polymerization	155
Many polymers	Depolymerization	50

B. *Nonaqueous Sonochemistry*

Until the past few years, very few examples of homogeneous nonaqueous sonications had been reported. These included the very slow degradation of a few common solvents (156) (CH_3CN and CCl_4), the initiation of explosions of tetranitromethane and nitroglycerine (157), the sevenfold acceleration (158) of the Curtius rearrangement of $\text{C}_6\text{H}_5\text{CON}_3$ to $\text{C}_6\text{H}_5\text{NCO}$ and N_2 , and the depolymerization of high molecular weight polymers (50). 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 cavitation collapse could only be supported in high tensile strength liquids such as water (159,160). As noted earlier, however, the problem is simply that many organic liquids have high vapor pressures, which greatly diminish the intensity of cavitation 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) (89,90,161,162). 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 (89). Other recent reports compare the sonolysis and pyrolysis of biacetyl (which gives primarily acetone) (163) and the sonolysis and radiolysis of menthone (164). Nonaqueous chemistry can be complex, however, as in the tarry polymerization of several substituted benzenes (165).

By the proper choice of solvent and experimental conditions (i.e., low volatility, highly stable liquids at low temperature: e.g., decane, -10°C), the rates of degradation of nonaqueous liquids can be made quite slow, well below those of water. This is of considerable advantage, since one may then observe the primary sonochemistry of dissolved substrates rather than secondary reactions with solvent fragments. 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. One may hope to see the increased use of low-volatility organic liquids in future sonochemical studies.

In addition, there are a few examples of heterogeneous nonaqueous sonochemistry, in both liquid-liquid and liquid-solid systems. Two recent reports have utilized ultrasonic agitation in place of or along with phase transfer catalysis: for the preparation of dichlorocarbene from aqueous $\text{NaOH}/\text{CHCl}_3$ (166), and for N-alkylation of amines with alkyl halides (167). Along the same lines, several papers have appeared in which

ultrasonic irradiation of liquid–solid reactions enhances rates and yields: (1) the deprotonation of dimethylsulfoxide by NaH slurries (168); (2) the preparation of thioamides from amides treated with solid P_4S_{10} (169); (3) the reduction of aryl halides to arenes with solid lithium aluminum hydride (170); (4) the oxidation of secondary alcohols to ketones with solid $KMnO_4$ (171); and (5) the synthesis of aromatic acyl cyanides from acid chlorides and solid KCN (172). The last of these had led on to an unusual, and unexplained, observation of reaction pathway switching during ultrasonic irradiation (173). 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.

V

ORGANOMETALLIC SONOCHEMISTRY

The effects of high-intensity ultrasound on organometallic systems is an area of only recent investigation; consequently, a limited range of complexes and 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 the metal or metal complex, 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.

A. Homogeneous Systems

1. Stoichiometric Reactions

In 1981, the first report on the sonochemistry of discrete organometallic complexes demonstrated the effect of ultrasound on iron carbonyls in alkane solutions (174). 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, for our present discussion we will focus upon it as an archetype. Thermolysis of $\text{Fe}(\text{CO})_5$, for example, gives pyrophoric, finely divided iron powder (175); ultraviolet photolysis (176) yields $\text{Fe}(\text{CO})_9$, via the intermediate $\text{Fe}(\text{CO})_4$; multiphoton infrared photolysis in the gas phase (177,178) yields isolated Fe atoms. Multiple ligand dissociation, generating $\text{Fe}(\text{CO})_3$, $\text{Fe}(\text{CO})_2$, etc., is not available from ordinary thermal or photochemical processes but does occur in matrix-isolated (179,180) and gas-phase laser (181,182) 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.

During sonolysis in alkane solvents in the absence of alternate ligands, the unusual clusterfication of $\text{Fe}(\text{CO})_5$ to $\text{Fe}_3(\text{CO})_{12}$ is observed, together with the formation of finely divided iron (174,183). 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 cavitation collapse and the maximum temperature reached during such collapse decreases with increasing solvent vapor pressure. Given this method for controlling the conditions generated during cavitation, we would also expect to see the ratio of products vary as a function of solvent vapor pressure. As shown in Fig. 11, this proves to be the case: the ratio of products can be varied over a 100-fold range, with the production of $\text{Fe}_3(\text{CO})_{12}$ strongly favored by increasing solvent volatility, as expected, since the sonochemical production of metallic iron requires greater activation energy than the production of $\text{Fe}_3(\text{CO})_{12}$.

In order to probe the nature of the reactive site generated during the cavitation event, one may examine the sonochemical rate as a function of the volatility of the *substrate* (63). If one fixes the total solution vapor pressure by using appropriate solvent mixtures and keeps the $\text{Fe}(\text{CO})_5$ concentration constant, but changes the $\text{Fe}(\text{CO})_5$ vapor pressure by changing the ambient temperature, the observed first order rate coefficient increases linearly with increasing substrate vapor pressure and has a non-zero intercept, as shown in Fig. 12. This is consistent with a two-site model of sonochemical reactivity: the linear dependence on substrate vapor pressure represents the sonochemistry occurring in the gas phase of the cavitation event, and the non-zero intercept demonstrates a liquid-phase sonochemical site, presumably a thin liquid shell surrounding the cavity, as shown in Fig. 5. The importance of substrate volatility is clear, since the predominant site of sonochemistry is gas phase.

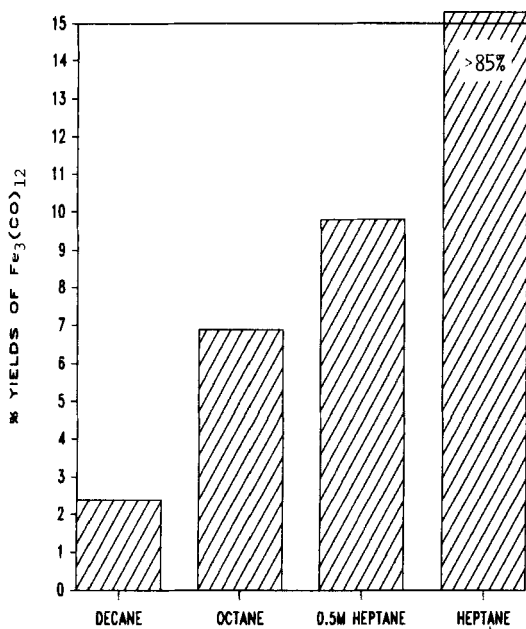


FIG. 11. Relative yields of $\text{Fe}_3(\text{CO})_{12}$ versus Fe metal with increasing solvent vapor pressure. [Plotted from data in Ref. 174.]

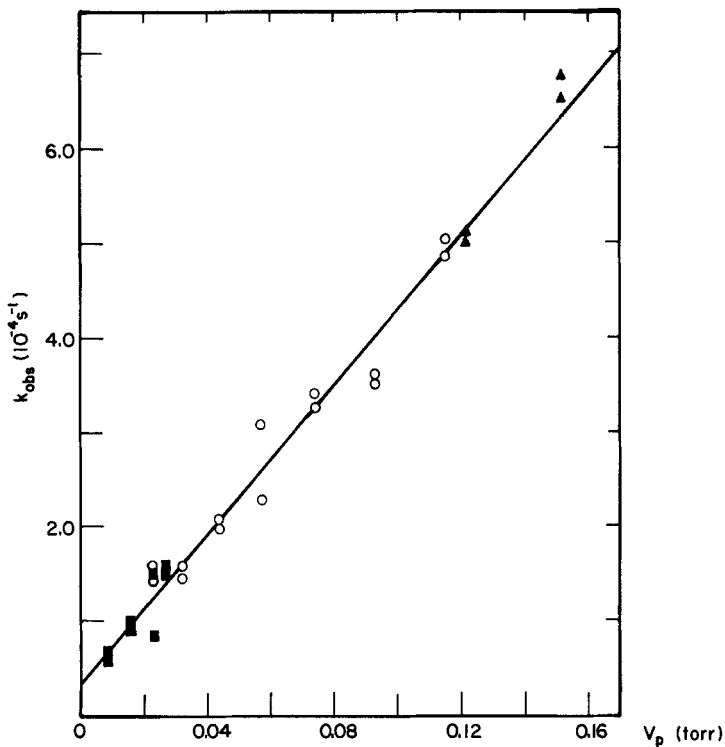
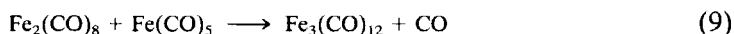
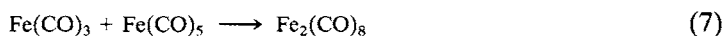
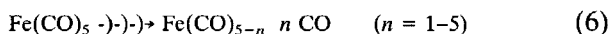
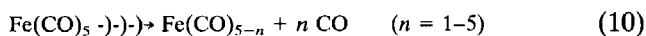


FIG. 12. First order sonochemical rate coefficients as a function of $\text{Fe}(\text{CO})_5$ vapor pressure. Total vapor pressure was 5.0 torr (63).

The proposed chemical mechanism by which $\text{Fe}_3(\text{CO})_{12}$ is formed during the sonolysis of $\text{Fe}(\text{CO})_5$ is shown in Eqs. (6)–(9). $\text{Fe}_2(\text{CO})_9$ is not generated during the synthesis of $\text{Fe}_3(\text{CO})_{12}$, and sonolysis of $\text{Fe}_2(\text{CO})_9$ yields only $\text{Fe}(\text{CO})_5$ and finely divided iron. The production of $\text{Fe}_3(\text{CO})_{12}$ arises from initial multiple dissociative loss of CO from $\text{Fe}(\text{CO})_5$ during cavitation, followed by secondary reactions with excess $\text{Fe}(\text{CO})_5$. Ligand trapping studies confirm the formation of $\text{Fe}(\text{CO})_3$, but cannot rule out the dimerization of $\text{Fe}(\text{CO})_4$ in the localized cavitation site. The reaction of the putative $\text{Fe}_2(\text{CO})_8$ with $\text{Fe}(\text{CO})_5$ may proceed through initial dissociation in analogy to the matrix isolation reactivity (184) of $\text{Fe}(\text{C}_4\text{H}_4)_2(\text{CO})_4$.



In addition to clusterification, ligand substitution also occurs for $\text{Fe}(\text{CO})_5$, and in fact for most metal carbonyls. This has proved useful as a mechanistic probe of the reactive species formed during cavitation. Sonication of $\text{Fe}(\text{CO})_5$ in the presence of phosphines or phosphites produces $\text{Fe}(\text{CO})_{5-n}\text{L}_n$ ($n = 1, 2$, and 3). The ratio of these products is independent of length of sonication; the multiply substituted products increase with increasing initial [L]; $\text{Fe}(\text{CO})_4\text{L}$ is *not* sonochemically converted to $\text{Fe}(\text{CO})_3\text{L}_2$ on the timescale of its production from $\text{Fe}(\text{CO})_5$. These observations are consistent with the same primary sonochemical event responsible for clusterification



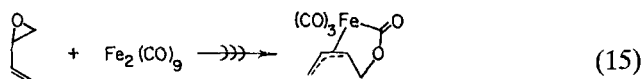
Sonochemical ligand substitution readily occurs with a variety of other metal carbonyls, as shown in Table IV. In all cases, multiple ligand substitution originates directly from the parent carbonyl. The rates of sonochemical ligand substitution of the various metal carbonyls follow their relative volatilities, as predicted from the nature of the cavitation 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 (185). Upon

TABLE IV
 HOMOGENEOUS ORGANOMETALLIC SONOCHEMISTRY

Reactants	Products	Ref.
Clusterification		
Fe(CO) ₅	Fe ₃ (CO) ₁₂ , Fe	174,183
Fe ₂ (CO) ₉	Fe, Fe(CO) ₅	174,183
Ligand substitution ^a		
Cr(CO) ₆ + L	Cr(CO) ₅ L, Cr(CO) ₄ L ₂ , Cr(CO) ₃ L ₃	183
Mo(CO) ₆ + L	Mo(CO) ₅ L, Mo(CO) ₄ L ₂	183
W(CO) ₆ + L	W(CO) ₅ L, W(CO) ₄ L ₂	183
Fe(CO) ₅ + L	Fe(CO) ₄ L, Fe(CO) ₃ L ₂ , Fe(CO) ₂ L ₃	174,183
FeCp(CO) ₂ I + L	FeCp(CO)(L)I	189
Fe ₂ (CO) ₉ + alkenylepoxide	Fe(CO) ₃ (π-allyllactone)	185
Fe ₃ (CO) ₁₂ + L	Fe(CO) ₄ L, Fe(CO) ₃ L ₂	174,183
Mn ₂ (CO) ₁₀ + L	Mn ₂ (CO) ₈ L ₂	183
Co(Cp) ₂ + CO	CoCp(CO) ₂	191
Sn ₂ R ₆	SnR ₃ ·, R·	193
Secondary reactions		
M ₂ (CO) ₁₀ + R ₃ CX	M(CO) ₅ X (M = Mn, Re; X = Cl, Br)	183
Co ₂ (CO) ₈ + alkane	Co ₂ (CO) ₆ (C ₂ H ₂), Co ₄ (CO) ₁₀ (C ₂ H ₂)	189
Sonocatalytic reactions		
Fe _x (CO) _y + 1-alkene	<i>cis</i> -, <i>trans</i> -2-Alkene	174,183
Ru _x (CO) _y + 1-alkene	<i>cis</i> -, <i>trans</i> -2-Alkene	183
Mo(CO) ₆ + 1-alkene	<i>cis</i> -, <i>trans</i> -2-Alkene	183
Co ₂ (CO) ₈ + 1-alkene	<i>cis</i> -, <i>trans</i> -2-Alkene	183

^a L = various phosphines and phosphites.

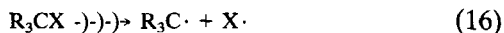


sonication in a cleaning bath, Fe₂(CO)₉ slurries in hydrocarbon solutions of alkenyl epoxides rearrange as shown in Eq. (15). The same reaction occurs thermally with Fe(CO)₄(tetrahydrofuran), indicating the probable intermediacy of a coordinatively unsaturated (or loosely coordinated) species upon sonication of Fe₂(CO)₉. The authors expressed surprise (185) that under the conditions Fe(CO)₅ and Fe₃(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 Fe₂(CO)₉ but which are *not* sufficient in

homogeneous solutions of $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$. Under more intense ultrasonic irradiation, $\text{Fe}(\text{CO})_5$, for example, will undergo substitution with alkenes (183).

The sonolysis of $\text{Mn}_2(\text{CO})_{10}$ makes for an interesting comparison (186), since either metal-metal (as in photolysis) (187) or metal-carbon (as in moderate temperature thermolysis) (188) bond breakage could occur. Ligand substitution will occur from either route producing the axially di-substituted $\text{Mn}_2(\text{CO})_8\text{L}_2$. Using benzyl chloride as a trap for the possible intermediacy of $\text{Mn}(\text{CO})_5$, the sonochemical substitution of $\text{Mn}_2(\text{CO})_{10}$ has been shown to follow the thermal, rather than the photochemical, pathway of dissociative CO loss.

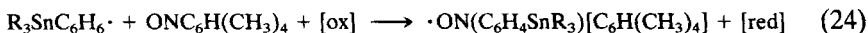
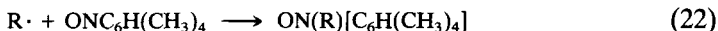
Upon sonication in halocarbon solvents, metal carbonyls undergo facile halogenations (186). The rates of halogenation are solvent dependent, but independent of choice of metal carbonyl or its concentration, and represent the products of secondary reactions occurring from the sonolytic decomposition of the halocarbon solvent, as shown in Eqs. (16)–(20). Alkanes and other halogen 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 $\text{Co}_2(\text{CO})_8$ in *n*-alkanes (C_5H_{12} through $\text{C}_{10}\text{H}_{22}$) (189). The principal products are $\text{Co}_2(\text{CO})_6(\text{C}_2\text{H}_2)$ and $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$, with small amounts of $\text{Co}_4(\text{CO})_{12}$. $\text{Co}_4(\text{CO})_{12}$ is an expected product, since it is easily formed upon pyrolysis of $\text{Co}_2(\text{CO})_8$. The acetylene of the former complexes originates from the solvent, as confirmed by isotope labeling. Their formation is initially quite surprising, until one notes that their rates of formation are comparable to the slow rate of C_2H_2 formation from sonolysis of the alkane (89) and that cobalt carbonyls undergo facile thermal reactions with alkynes (190). Thus, the origin of this sonochemical alkane activation is *not* in some high energy organometallic fragment, but in 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 (189). In preliminary studies of the metal-

locenes (191), $\text{Co}(\text{Cp})_2$ has been found to undergo facile ligand substitution during sonication under CO to yield $\text{Co}(\text{Cp})(\text{CO})_2$. This reaction under simple thermal conditions (192) 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 (193). Trapping of intermediate radicals by nitroso-durene and analysis by ESR demonstrated alkyl–tin bond cleavage during sonication in benzene solutions. The following reaction scheme [Eqs. (21)–(24)] 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.



2. 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 (176,194). The thermal (195–197) and photochemical (198–202) isomerization of terminal olefins by metal carbonyls have been extensively studied, and provide a useful test case for applications of sonocatalysis.

As shown in Fig. 13, a variety of metal carbonyls upon sonication will catalyze the isomerization of 1-pentene to *cis*- and *trans*-2-pentene (186). Initial turnover rates are about 1–100 mol 1-pentene isomerized/mol of precatalyst/hour, and represent rate enhancements of $\sim 10^5$ over thermal controls (174). The relative sonocatalytic and photocatalytic activities of these carbonyls are in general accord. An exception is $\text{Ru}_3(\text{CO})_{12}$, which is

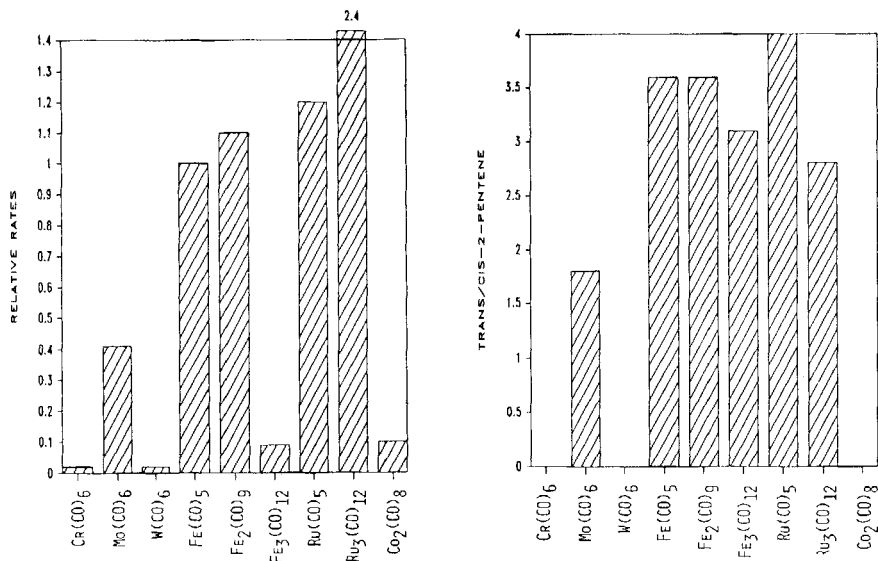
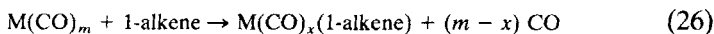
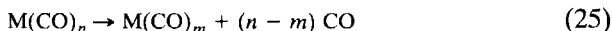
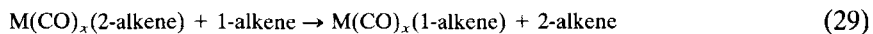
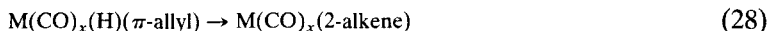
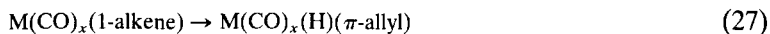


FIG. 13. Relative rates and trans/cis ratios of the sonocatalysis of 1-pentene isomerization by metal carbonyls. [Plotted from data in Ref. 183.]

relatively more active as a sonocatalyst and shows very different trans/cis ratios under sonolysis; it appears that the catalytic agent produced sonochemically in this case is not that produced photochemically (186). A variety of terminal alkenes will serve as substrates for sonocatalytic isomerization, although increasing steric hindrance, as in 2-ethyl-pent-1-ene and allylbenzene, significantly diminishes the observed rates. Alkenes without β -hydrogens will not serve as substrates, in contrast to the radical chain isomerization of maleic acid which occurs upon ultrasonic irradiation of aqueous Br_2 solutions (132,133).

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 (197) and photochemical systems (195). 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 Eqs. (25)–(29). In keeping with this scheme, sonication of $\text{Fe}(\text{CO})_5$ in the presence of 1-pentene and CO does produce $\text{Fe}(\text{CO})_4(\text{pentene})$, as determined by FTIR spectral stripping (183).



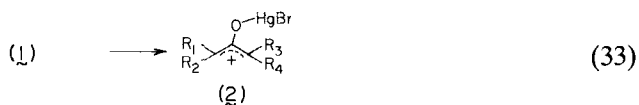
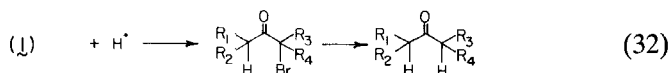
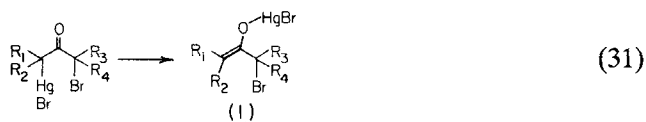
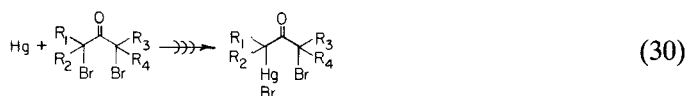


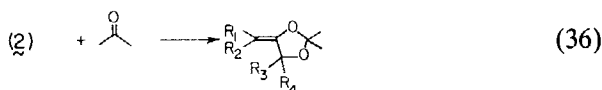
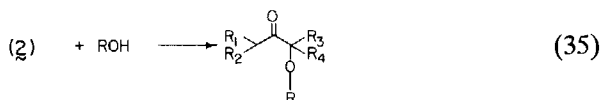
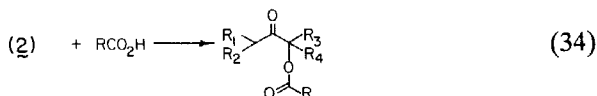
B. Heterogeneous Systems

1. Stoichiometric Reactions

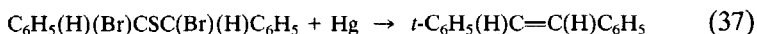
The use of ultrasound to accelerate chemical reactions in heterogeneous systems is becoming increasingly widespread. The physical phenomena which are responsible include the creation of emulsions at liquid-liquid interfaces, the generation of cavitation erosion and cleaning at liquid-solid interfaces,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

In organometallic chemistry, the use of ultrasound in liquid-liquid heterogeneous systems has been limited to Hg. The emulsification of Hg with various liquids dates to the very first reports on sonochemistry (3,203,204). The use of such emulsions for chemical purposes, however, was delineated by the extensive investigations of Fry and co-workers (205-212), who have reported the sonochemical reaction of various nucleophiles with α,α' -dibromoketones and mercury. The versatility of this reagent is summarized in Eqs. (30)-(36).





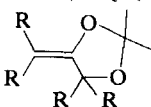
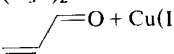
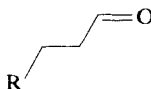
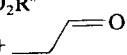
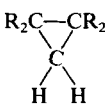
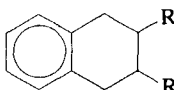
There are synthetic advantages to the use of ultrasound in these systems. For example, such Hg dispersions allow reactions with more sterically hindered ketones yet introduces only one nucleophilic group even in sterically undemanding systems (209). In addition, the reaction given in Eq. (36) represents a convenient one-step synthesis of 1,3-dioxolans (206). 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 (205), 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 Eq. (37); the mechanism by which this occurs is unclear, particularly since no thiobenzaldehyde or 1,2-diphenylthiirane is formed (212). One might speculate that an internal Wurtz coupling is the initial step, forming 1,2-diphenylthiirane, which is rapidly desulfurized to *trans*-stilbene.



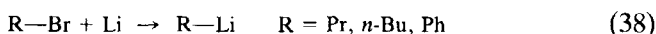
The effects of ultrasound on liquid–solid heterogeneous organometallic reactions has been a matter of intense recent investigation, particularly in the laboratories of Luche, Boudjouk, and Ishikawa. The first use of ultrasound to prepare organometallic complexes of the main group metals (e.g., lithium, magnesium, and aluminum) from organic halides, however, originates in the seldom cited work of Renaud (213). 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.

The report by Luche and Damiano in 1980 of the use of an ultrasonic cleaner to accelerate lithiation reactions (214) initiated the recent interest.

TABLE V HETEROGENEOUS ORGANOMETALLIC SONOCHEMISTRY

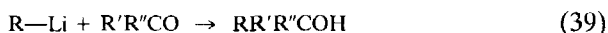
Organic reactant	Product	Ref.
Hg (R ₂ BrC) ₂ CO + R'CO ₂ H (R ₂ BrC) ₂ CO + R'OH	(HR ₂ C)CO[C(O ₂ CR')R ₂] (HR ₂ C)CO[C(OR')R ₂]	205,207-210 211
(R ₂ BrC) ₂ CO + (H ₃ C) ₂ CO		206
C ₆ H ₅ (H)(Br)CSC(Br)(H)C ₆ H ₅	<i>t</i> -C ₆ H ₅ (H)C=C(H)C ₆ H ₅	212
Mg R—Br R—Br + Al	R—MgBr AlR ₃	213,242 213
Li R—Br R = (<i>n</i> -Pr, <i>n</i> -Bu, Ph) R—Br + R'R''CO R—Br + (H ₃ C) ₂ NCHO R—Br +  + Cu(I)	R—Li RR'R''COH RCHO 	214 214,215 216 217
R ₃ M—Cl (M = C, Si, Sn; R = alkyl, aryl) R ₃ SiCl ₂ (R = arenes)	R ₃ MMR ₃ <i>cyclo</i> -(R ₂ Si) ₃	218,219 219,224
Na Arenes	Na(arene ⁻)	225-227
K XH ₂ C—(CH ₂) _n —CH ₂ X	Cycloalkanes	228
LiAlH ₄ R ₃ M—Cl (M = Si, Ge, Sn; X = Cl, NR ₂ , OR)	R ₃ M—H	220
Zn CF ₃ I + RR'C=O CF ₃ I + R—Br + Pd(0) CF ₃ I + RC≡CR + Cu(0) RR'C=O + BrCH ₂ CO ₂ R'' R—Br + Li + ZnBr ₂ +  H ₂ Cl ₂ + R ₂ C=CR ₂	RR'C(OH)CF ₃ R—CF ₃ HRC=CR(CF ₃) RR'C(OH)CH ₂ CO ₂ R'' R—CH ₂ —CH ₂ —CH ₂ —CHO 	229 232 233 230 235,236 237
1,2-(BrH ₂ C) ₂ C ₆ H ₄ + dienophiles		238,239
Transition metals RuCl ₃ + Zn + 1,5-cyclooctadiene	(η ⁶ -1,3,5-cyclooctadiene)- (η ⁴ -1,5-cyclooctadiene)Ru(0)	240
MCl ₅ + Na + CO (M = V, Nb, Ta)	M(CO) ₆ ⁻	243
MCl ₆ + Na + CO (M = Cr, Mo, W)	M ₂ (CO) ₁₀ ²⁻	243
MnCl ₃ + Na + CO	Mn(CO) ₅ ⁻	243
FeCl ₃ + Na + CO	Fe(CO) ₄ ²⁻ + Fe ₂ (CO) ₈ ²⁻	243
NiCl ₂ + Na + CO	Ni ₆ (CO) ₁₂ ²⁻	243
Co(acac) ₃ + C ₅ H ₆ + COD + Mg/C ₁₄ H ₁₀	Co(Cp)(COD)	247

Excellent yields of organolithium compounds were found for *n*-propyl-, *n*-butyl-, and phenyllithium (61–95%), even at room temperature in wet solvents [Eq. (38)], which has potential utility for large-scale industrial



applications. Lithiation of isopropyl and *t*-butyl bromides remained sluggish, however.

More impressive is the striking improvement which sonication afforded to the Barbier reaction [Eq. (39)] (214). This one-step coupling of organic

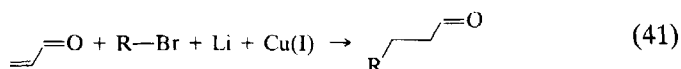


halides with carbonyl compounds via magnesium or lithium intermediates is significantly hastened (10–40 minutes) with excellent yields (76–100%) for a wide range of organobromides (including *t*-butyl and benzyl) and a variety of ketones or aldehydes. This has proved to be the method of choice in the synthesis of complex cyclopentanones via an intramolecular Barbier reaction (215).

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 [Eq. (40)] suffers from side reactions and low yields.

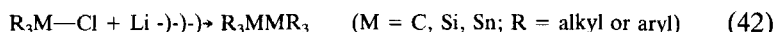


Upon sonication in a cleaning bath, mixtures of organic halides, dimethylformamide, and lithium sand in THF give very good yields (67–88%) of aldehydes, although no direct comparison to the simple thermal reaction was made (216). Similar improvements in yields are observed in organocopper conjugate alkylations of enones [Eq. (41)] (217). The formation of the organocopper reagent was accomplished by ultrasonic irradiation of



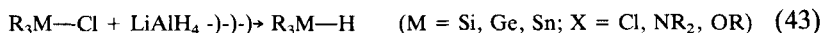
alkyl or aryl bromide solutions in the presence of lithium sand and a solution of a Cu(I) salt; temperature control during the sonication is quite important in these reactions to avoid Barbier-type α -alkylations.

Wurtz-type couplings have also been observed upon sonication of lithium in the presence of both organic halides (yields 36–73%) (218) and chlorosilanes or chlorostannanes (yields 42–94%) [Eq. (42)] (219).

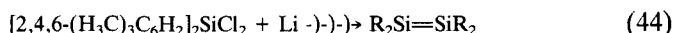


Lithium wire is acceptable (but higher yields result with lithium sand dispersed in mineral oil) and requires in some cases a small amount of

anthracene as electron transfer catalyst. Direct comparisons to reactions run without ultrasound, but under high speed stirring or heating, were not made. In the same vein, the use of low intensity ultrasound for the preparation of main group hydrides from the reaction of the corresponding chlorides with lithium aluminum hydride [Eq. (43)] has been recently reported (220).



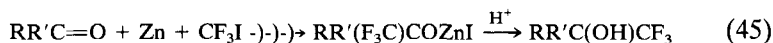
In the case of dichlorosilanes, oligomerization to form cyclopolysilanes occurs in high yields, with the product's ring size dependent upon the steric bulk of the starting silane (219). Boudjouk initially reported (221) the synthesis of West's novel disilene (222) upon sonication of lithium with the highly hindered bis(mesityl)dichlorosilane [Eq. (44)]. It is difficult, however, to obtain consistent results with this sonochemical synthesis of the



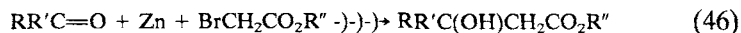
disilene (223), and the generally observed product is the hexamesityl-cyclotrisilane (224).

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 (225) and to give higher yields with greater control in the synthesis of phenylsodium (226). 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 (227). 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 for other reactions (228).

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 [Eq. (45)] (229). In this case the choice of

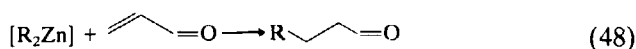
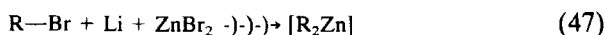


metal was dictated by the relative stability of the perfluoroalkylzinc compounds compared to the corresponding magnesium or lithium species. Good yields (45–86%) were reported for the formation of alcohols from the sonication in a cleaning bath of a mixture of Zn powder with CF_3I in dimethylformamide solutions of several ketones and aldehydes. The closely related Reformatsky reaction [Eq. (46)] has also proven to be



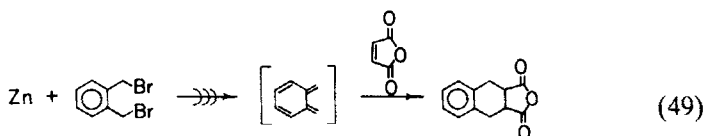
assisted by low intensity ultrasound (230). Extensive comparison to alternative reaction conditions was made in this thorough study. The use of I_2 or I^- promoters and dioxane as solvent is important for optimal yields. Sonication provided reaction rates and yields (typically 30 minutes and >90% yield) as good or better than the use of activated zinc powders (231) prepared from the reduction of anhydrous $ZnCl_2$. The use of ultrasonically generated organozinc complexes for perfluoroalkylation of allyl, vinyl, and aryl halides with $Pd(0)$ (232) catalyst and of alkynes with $Cu(0)$ catalyst (233) has also been reported.

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 [Eqs. (47) and (48)] (234,235). 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 cavitation effects were probably not involved since such solvents supposedly preclude the occurrence of cavitation (234). 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 (235). 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 (236).

Low intensity ultrasound has also been applied to the Simmons–Smith cyclopropanation of olefins with zinc–diiodomethane (237). This reaction normally will not occur without activation of mossy Zn with I_2 or Li, and was difficult to scale-up due to delayed initiation. Yields upon sonication 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 [Eq. (49)],

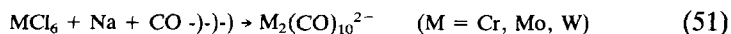


which has been trapped by a variety of dienophiles (238). This has found synthetic application in the synthesis of functionalized hexa-hydro-anthracenes and -naphthalenes (239).

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 (240). The use of ultrasound in simple reductions using Zn are a likely area for further development.

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 cavitation shock waves and microstreaming are also important contributions. 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 (241), 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 (242).

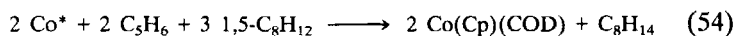
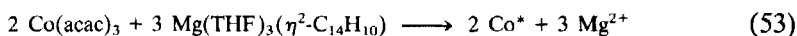
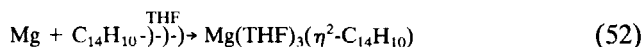
The activation of less reactive metals remains an important goal which continues to attract major efforts in heterogeneous catalysis, metal vapor chemistry, and organometallic synthesis. Given the extreme conditions generated by acoustic cavitation at surfaces, analogies to autoclave conditions or to metal vapor reactors are not inappropriate. In order to probe the potential generality of ultrasonic activation of heterogeneous reactions, Suslick and Johnson examined (243) 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 (244,245) the formation of the early transition metal carbonyls still require "bomb" conditions (100–300 atm of CO, 100–300°C) (246). 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, 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 [Eqs. (50) and (51)]. 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}C 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 cavitation microjets, 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 (243). In the case of the reduction of WCl_6 , sonication under CO showed the initial formation of tungsten carbonyl halides, followed by conversion of $\text{W}(\text{CO})_6$, and finally its further reduction to $\text{W}_2(\text{CO})_{10}^{2-}$. Thus, the reduction process appears to be sequential: reactive species formed upon partial reduction are trapped by CO.

Another recent application to the activation of transition metals was reported (247) by Bönemann, Bogdavic, and co-workers, in which an extremely reactive Mg species was used to reduce metal salts in the presence of cyclopentadiene, 1,5-cyclo-octadiene, and other ligands to form their metal complexes. The reactive Mg species, characterized as $\text{Mg}(\text{THF})_3$ (anthracene), was produced from Mg powder in THF solutions containing a catalytic amount of anthracene by use of an ultrasonic cleaning bath. A plausible scheme for this reaction has been suggested:



2. 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 (248), 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 10-fold). The effect of irradiating operating catalysts owes much simply to improved mass transport (249). In addition, increased dispersion during the formation of catalysts under ultrasound (250) [e.g., Ziegler–Natta polymerizations (251)] will enhance reactivity, as will the fracture of friable solids [e.g., noble metals on carbon or silica (191) or malleable metals (252)]. In the case of bulk metal catalysts, the removal of passivating coatings through surface cavitation damage is well established (253–255).

The range of reactions which have been examined is wide (248) and includes hydrogenations (256), ammonia synthesis (257), polymerizations (251), and oxidations (258). 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 (259), the hydrogenation of olefins by formic acid with Pd on carbon (260), and the hydrosilation of 1-alkenes by Pt on carbon (261).

VI

CONCLUDING REMARKS

The use of ultrasound in both homogeneous and heterogeneous reactions will see increasing study. The potential to do high energy chemistry in condensed phases at room temperature remains an attractive feature of sonochemistry. Unique examples of sonochemical reactivity quite different from thermal or photochemical processes have been noted. There are analogies to shock wave and gas-phase pyrolyses, to “bomb” reactions, and to metal vapor chemistry, which will continue to be explored. The use of ultrasound in the synthesis of organometallic species has had particular impact in heterogeneous systems and no doubt will find application in nearly any case where interphase mixing is a problem.

A primary limitation of sonochemistry 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 cavitation collapse, which permit the variation of product distributions in a rational fashion.

Early in the study of cavitation phenomenon, Minnaert observed that scientists

have hardly ever investigated the sounds of running water. As a matter of fact we know very little about the murmur of the brook, the roar of the cataract, or the humming of the sea [Ref. 34].

Be this as it may, we *are* gaining a significant understanding of the chemical consequences of such!

ACKNOWLEDGMENTS

The author sincerely appreciates the efforts of his graduate students and postdoctoral research associates, whose efforts are irreplaceable. In particular, this review has been greatly assisted by D. J. Casadonte, E. B. Flint, D. A. Hammerton, and L. J. Hogenson. The detailed suggestions of Professor J. L. Luche require special thanks. The generosity of funding from the National Science Foundation, the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The author is a Sloan Foundation Research Fellow and the recipient of a Research Career Development Award of the National Institutes of Health.

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