Chapter 12

Sonochemistry of Organometallic Compounds

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The chemical effects of ultrasound are reviewed with a focus on organometallic systems. Acoustic cavitation is the principal source of sonochemistry, but its nature is quite dependent on the local environment. Cavitational collapse in homogeneous liquids generates hot spot heating of ≈5200K, which can cause multiple ligand dissociation, clusterification, and initiation of homogeneous catalysis. Cavitation near solids has much different effects due to microjet impact on the surface; enhancement of a wide variety of liquid-solid reactions and heterogeneous catalysis occur. These unusual reaction patterns are compared to other high energy processes.

The purpose of this chapter will be to serve as a critical introduction to the nature and origin of the chemical effects of ultrasound. We will focus on organo-transition metal sonochemistry as a case study. There will be no attempt to be comprehensive, since recent, exhaustive reviews on both organometallic sonochemistry (1) and the synthetic applications of ultrasound (2) have been published, and a full monograph on the chemical, physical and biological effects of ultrasound is in press (3).

The chemical and biological effects of ultrasound were first reported by Loomis more than 50 years ago (4). Within fifteen years of the Loomis papers, widespread industrial applications of ultrasound included welding, soldering, dispersion, emulsification, disinfection, refining, cleaning, extraction, flotation of minerals and the degassing of liquids (5),(6). The use of ultrasound within the chemical community, however, was sporadic. With the recent advent of inexpensive and reliable sources of ultrasound, there has been a resurgence of interest in the chemical applications of ultrasound.

A number of terms in this area will be unfamiliar to most chemists. Cavitation is the formation of gas bubbles in a liquid and occurs when the pressure within the liquid drops significantly below the vapor pressure of the liquid. Cavitation can occur from a variety of causes: turbulent flow, laser heating, electrical discharge, boiling, radiolysis, or acoustic irradiation. We will be concerned

exclusively with <u>acoustic cavitation</u>. When sound passes through a liquid, it consists of expansion (negative-pressure) waves and compression (positive-pressure) waves. These cause pre-existing bubbles to grow and recompress. Acoustic cavitation can lead, as discussed later, to implosive bubble collapse and associated high-energy chemistry. To indicate ultrasonic irradiation ("sonication"), we will use as our symbol: -)-)-)→. <u>Sonocatalysis</u> will be restricted in its use only to the creation of a catalytically competent intermediate by ultrasonic irradiation; we will not refer to a simple sonochemical rate enhancement of an already ongoing reaction by this term.

Mechanisms of the Chemical Effects of Ultrasound

Ultrasound spans the frequencies of roughly 20 KHz to 10 MHz (human hearing has an upper limit of <18 KHz). Since the velocity of sound in liquids is ≈1500 m/sec, ultrasound has acoustic wavelengths of roughly 7.5 to 0.015 cm. Clearly no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry. Instead, the chemical effects of ultrasound derive from several different physical mechanisms, depending on the nature of the system.

The most important of these is acoustic cavitation, which involves at least three discrete stages: nucleation, bubble growth, and, under proper conditions, implosive collapse. The dynamics of cavity growth and collapse are strikingly dependent on local environment, and cavitation in a homogeneous liquid should be considered separately from cavitation near an interface.

The tensile strength of a <u>pure</u> liquid is determined by the attractive intermolecular forces which maintain its liquid state; the calculated tensile strength of water, for example, is in excess of -1000 atmospheres (7). In practice however, the measured threshold for initiation of cavitation is never more than a small fraction of that. 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! Cavitation is initiated at a nucleation site where the tensile strength is dramatically lowered, such as small gas bubbles and gas filled crevices in particulate matter, which are present in the liquid.

The relevant question for the chemist lies in the actual phenomena responsible for sonochemical reactions. In homogeneous media, the generally accepted sonochemical mechanism involves pyrolysis by a localized "hot-spot" due to the adiabatic heating which is produced by the implosive collapse of a bubble during cavitation. A recent measurement of the temperature generated during this implosive collapse, which we will discuss in detail later, established that the effective temperature in the gas phase reaction zone is ≈5200°K with pressures of hundreds of atmospheres (8)!

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 do cavities implode spherically. Instead, a markedly asymmetric collapse occurs, which generates a jet of liquid directed at the surface, as seen in high speed micro-cinematography by Ellis (9) and Lauterborn (10) (shown

schematically in Figure 1). The jet velocities are greater than 100 m/sec. The origin of this jet formation is essentially a shaped-charge effect. The impingement of this jet can create a localized erosion (and even melting) responsible for surface pitting and ultra-sonic cleaning (11). A second contribution to erosion created by cavitation involves the impact of shock waves generated by the implo-sive collapse. The magnitude of such shock waves can be as high as 10^4 atmospheres, which will easily produce plastic deformation of malleable metals (12). The relative magnitudes of these two effects depends heavily on the specific system under consideration.

Acoustic streaming is another non-linear acoustic phenomenon important to the effect of ultrasound on surfaces (13). 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 due to acoustic streaming. This will occur even when the sound field is a stable standing wave in the absence of cavitation.

Enhanced chemical reactivity of solid surfaces are associated with these processes. The cavitational erosion generates unpassivated, highly reactive surfaces; it causes short-lived high temperatures and pressures at the surface; it produces surface defects and deforma-tions; 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.

Experimental Considerations

A variety of devices have been used for ultrasonic irradiation of solutions. The two most commonly in use are the ultrasonic cleaning bath and the direct immersion ultrasonic horn. In both 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 (usually 15 to 50 KHz). In general we find that the typical cleaning bath does not have sufficient acoustic intensities for most chemical applica-tions, with the exception of reactions involving extremely reactive metals (e.g., lithium). For this reason, we have adapted a much more intense source, the direct immersion ultrasonic horn, for inert atmo-sphere work (shown in Figure 2) and for moderate pressures (<10 atm.). These configurations may be used for both homogeneous and hetero-geneous sonochemistry. Ultrasonic horns are available from several manufacturers (14) at modest cost and are used primarily by biochem-ists 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 varied; the acoustic frequency is well-controlled, albeit fixed (typically at 20 KHz). Since power levels are quite high, counter-cooling of the
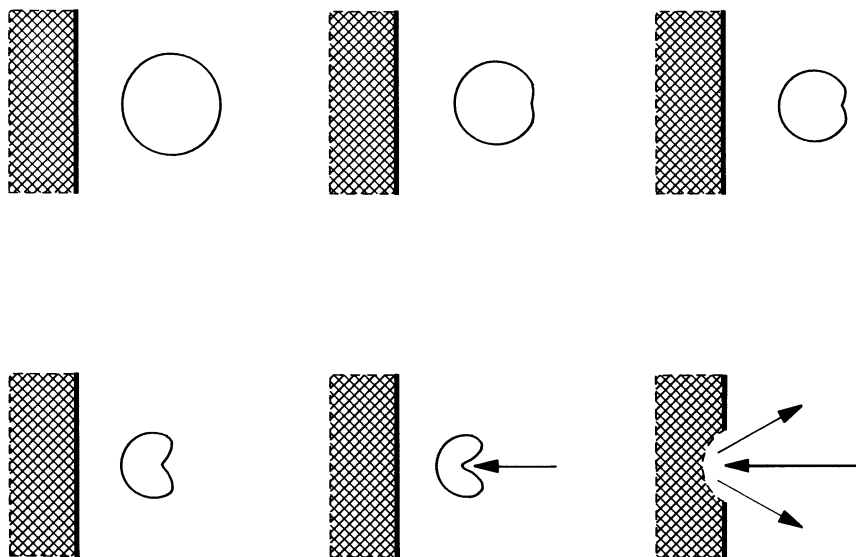
Figure 1. Cavitation Near a Surface. The sequence of a single bubble
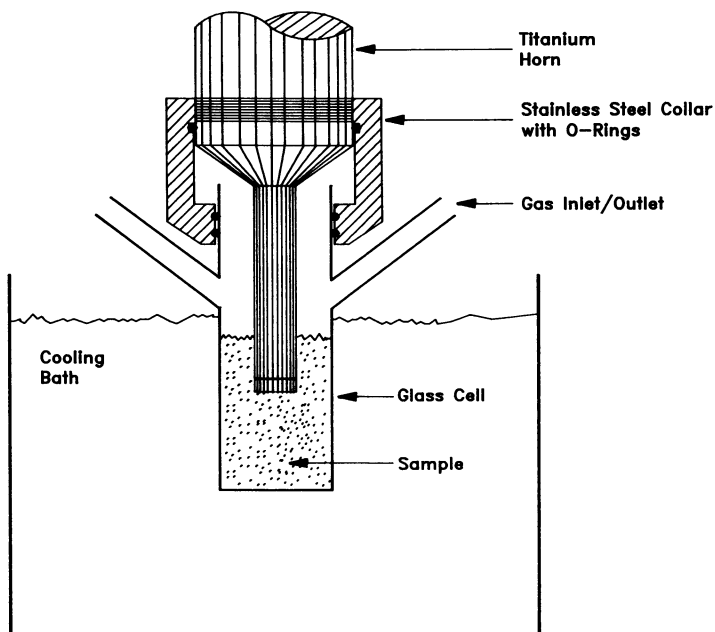collapsing follows from left to right, top to bottom.

Figure 2.   Direct Immersion Ultrasonic Horn Equipped for Inert
Atmosphere Work.

reaction solution is essential to provide temperature control; cooling
of the piezoelectric ceramic may also be necessary, depending on the
specific apparatus. 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. Alternatively, a thin teflon membrane can be
used to separate the Ti horn from the reaction solution.

A rough, but useful, comparison between typical sonochemical and
photochemical efficiencies is shown in Table 1. Homogeneous sono-
chemistry is typically _more_ efficient than photochemistry, and
heterogeneous sonochemistry is better still by several orders of
magnitude. Unlike photochemistry, whose energy inefficiency is
inherent in the production of photons, ultrasound can be produced with
nearly perfect efficiency from electric power. Still, a primary
limitation of sonochemistry remains its energy inefficiency: only a
small fraction of the acoustic power is 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.

Table I. Comparisons Between Sonochemical
and Photochemical Apparatuses

	Photochemistry	Homogeneous Sonochemistry	Heterogeneous Sonochemistry
Source	250W Quartz-Halogen	200W Cell Disrupter (at 60% power)	200W Cleaning Bath
Approximate Cost (1986)	$1800	$1900	$700
Typical Rates	7 µmol/min	10 µmol/min	500 µmol/min
Electrical Efficiency	2 mmol/KWH	5 mmol/KWH	200 mmol/KWH

Large-scale ultrasonic irradiations are extant technology. Liquid
processing rates of >200 L/min are routinely accessible from a variety
of modular, flow reactors with acoustic powers of tens of KW per unit
(14). 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. While these
units are of limited use for most laboratory research, they are of
potential importance in eventual industrial application of
sonochemical reactions.

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 cavitational hot spot mechanism. A few
of the more surprising results are mentioned here, but the reader is
referred to one of the recent reviews (1-3) for further details.

The frequency of the sound field is almost irrelevant to most
sonochemistry. Unlike photochemistry, there is no direct coupling of
the irradiating field with the molecular species ·in sonochemistry.
The effect of changing sonic frequency is simply one of altering the
resonant size of the cavitation event. The overall chemistry is
therefore little influenced over the range where cavitation can occur
(from tens of Hz to a few MHz) (15). The effect of the bulk solution
temperature lies primarily in its influence on the bubble content
before collapse. With increasing temperature, in general, sonochem-
ical 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 (16),(17). When secondary reactions
are being observed ·(as in corrosion or other thermal reactions
occurring after initial sonochemical events), temperature can play its
usual role in thermally activated chemical reactions. The maximum
temperature reached during cavitation is strongly dependent on the
ambient gas. Both its polytropic ratio ($\gamma = C_p/C_v$, which defines the
amount of heat released during the adiabatic compression of that gas)
and the thermal conductivity (which controls the degree to which the
collapse is adiabatic) have a dramatic impact, so that even the noble
gases affect cavitation differently. By the use of these variables,
one can fine-tune the energetics of cavitation, and hence exercise a
good measure of control over sonochemical reactions.

Homogeneous Sonochemistry

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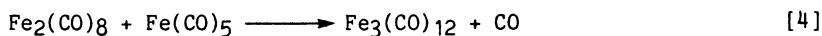because of the distinct nature of the cavitation event in each case.

In 1981, we first reported on the sonochemistry of discrete
organometallic complexes and demonstrated the effects of ultrasound on
metal carbonyls in alkane solutions (18). 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 acoustic cavitation can induce, and (because of space
limitations in this review) we will focus upon it as an archetype.

Thermolysis of $Fe(CO)_5$, for example, gives pyrophoric, finely
divided iron powder (19); ultraviolet photolysis (20) yields $Fe_2(CO)_9$,
via the intermediate $Fe(CO)_4$; multiphoton infrared photolysis in the
gas-phase (21),(22) yields isolated Fe atoms. Multiple ligand

dissociation, generating $Fe(CO)_3$, $Fe(CO)_2$, etc., is not available from ordinary thermal or photochemical processes (but does occur in matrix isolated (23),(24) and gas phase laser (25),(26) photolyses). These observations reflect the dual difficulties inherent in creating controlled multiple ligand dissociation: first, to deliver sufficient energy in a utilizable form and, second, to quench the highly energetic intermediates before complete ligand loss occurs.
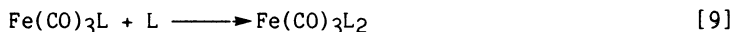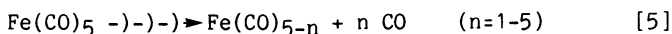
Sonolysis of $Fe(CO)_5$ in alkane solvents in the absence of alternate ligands causes the unusual clusterification to $Fe_3(CO)_{12}$, together with the formation of finely divided iron (18),(27). The rate of decomposition is cleanly first order, and the log of the observed first order rate coefficient is linear with the solvent vapor pressure. This is consistent with a simple dissociation process activated by the intense local heating generated by acoustic cavitation. As discussed earlier, the intensity of the cavitational collapse and the maximum temperature reached during such collapse decreases with increasing solvent vapor pressure. Thus, we would also expect to see the ratio of products change as a function of solvent vapor pressure. This proves to be the case: the ratio of products can be varied over a 100-fold range, with the production of $Fe_3(CO)_{12}$ strongly favored by increasing solvent volatility, as expected, since the sonochemical production of metallic iron requires greater activation energy than the production of $Fe_3(CO)_{12}$.

The proposed chemical mechanism by which $Fe_3(CO)_{12}$ is formed during the sonolysis of $Fe(CO)_5$ is shown in Equations 1 - 4.

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

$$Fe(CO)_3 + Fe(CO)_5 \longrightarrow Fe_2(CO)_8 \qquad [2]$$

$$2\ Fe(CO)_4 \longrightarrow Fe_2(CO)_8 \qquad [3]$$

$$Fe_2(CO)_8 + Fe(CO)_5 \longrightarrow Fe_3(CO)_{12} + CO \qquad [4]$$
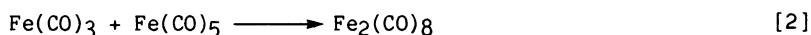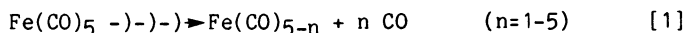
$Fe_2(CO)_9$ is not generated during the synthesis of $Fe_3(CO)_{12}$, and sonolysis of $Fe_2(CO)_9$ yields only $Fe(CO)_5$ and finely divided iron. In this mechanism, the production of $Fe_3(CO)_{12}$ arises from initial multiple dissociative loss of CO from $Fe(CO)_5$ during cavitation, followed by secondary reactions with excess $Fe(CO)_5$. The reaction of the putative $Fe_2(CO)_8$ with $Fe(CO)_5$ may proceed through initial dissociation in analogy to the matrix isolation reactivity (28) of $Fe(C_4H_4)_2(CO)_4$.

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

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

$$Fe(CO)_4 + L \longrightarrow Fe(CO)_4L \qquad\qquad [6]$$

$$Fe(CO)_3 + L \longrightarrow Fe(CO)_3L \qquad\qquad [7]$$

$$Fe(CO)_3 + CO \longrightarrow Fe(CO)_4 \qquad\qquad [8]$$

$$Fe(CO)_3L + L \longrightarrow Fe(CO)_3L_2 \qquad\qquad [9]$$

We have also observed sonochemical ligand substitution with a variety of other metal carbonyls (27),(29). In all cases, multiple ligand substitution occurs directly from the parent carbonyl. In fact, we have been able to use these reactions as probes of the nature of the reaction conditions created during acoustic cavitation. In order to probe the nature of the sonochemical hot spot, we determined the first order rate coefficients of sonochemical ligand substitution as a function of metal carbonyl vapor pressure. However, the efficacy of cavitational collapse and the temperatures so generated are strongly dependent on the vapor pressure of the solvent system (16),(17). Therefore, sonochemical substitutions at various ambient temperatures were done in solutions of two n-alkanes which had been mixed in the proper proportion to keep the total system vapor pressure constant (at 5.0 torr). In this fashion, the first order rate coefficients were determined as a function of metal carbonyl vapor pressure, for several metal carbonyls. In all cases the observed sonochemical rate coefficient increases linearly with increasing dosimeter vapor pressure and has a non-zero intercept. The linear dependence of the observed rate coefficients on metal carbonyl vapor pressure is expected for reactions occurring in the gas phase: as the dosimeter vapor pressure increases, its concentration within the gas phase cavity increases linearly, thus increasing the observed sonochemical rate coefficients. In addition, the non-zero intercept indicates that there is a vapor pressure <u>independent</u> component of the overall rate. There must be, therefore, an additional reaction site occurring within the liquid phase, presumably in the thin liquid shell surrounding the collapsing cavity (30),(31).

Our data can be used to estimate the effective temperatures reached in each site through comparative rate thermometry, a technique developed for similar use in shock tube chemistry (32). Using the sonochemical kinetic data in combination with the activation parameters recently determined by high temperature gas phase laser pyrolysis (33), the effective temperature of each site can then be calculated (8),(34): the gas phase reaction zone effective temperature is 5200 ± 650°K, and the liquid phase effective temperature is ≈1900°K. Using a simple thermal conduction model, the liquid reaction zone is estimated to be ≈200 nm thick and to have a lifetime of less than 2 μsec, as shown in Figure 3.

<u>Initiation of Homogeneous Catalysis.</u> Having demonstrated that ultrasound can induce ligand dissociation, the initiation of homogeneous catalysis by ultrasound becomes practical. The potential
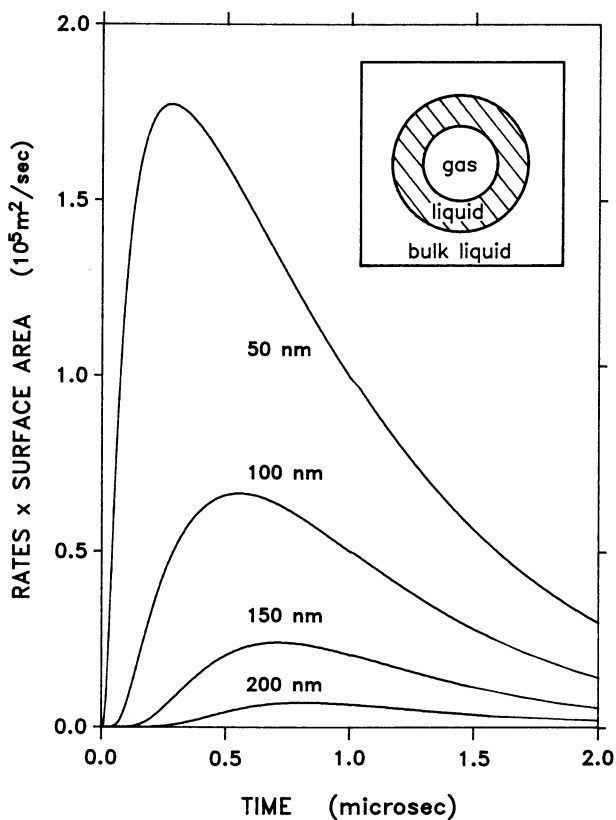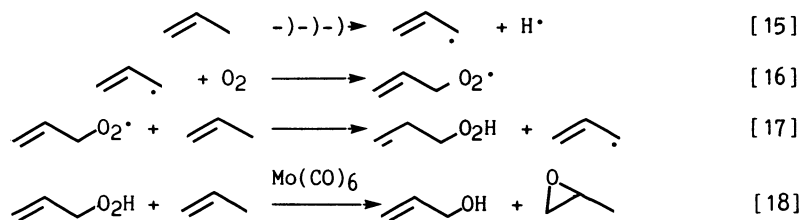
Figure 3. Temporal and Spatial Evolution of Reaction Rates in the Liquid Phase Reaction Zone. Rates were calculated as a function of time and distance from the bubble surface assuming only conductive heat transport from a sphere with radius 150µm at 5200K, embedded in an infinite matrix at 300K.

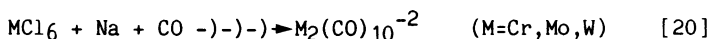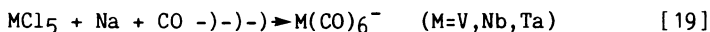advantages of such sonocatalysis include 1) the use of low ambient temperatures to preserve thermally sensitive substrates and to enhance selectivity, 2) the ability to generate high-energy species unobtainable from photolysis or simple pyrolysis, 3) the mimicry, on a microscopic scale, of bomb reaction conditions, and 4) the potential 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 (35).

A variety of metal carbonyls upon sonication will catalyze the isomerization of 1-alkenes to the internal alkenes (18),(27). Initial turnover rates are as high as 100 mol alkene isomerized/mol of precatalyst/h, and represent rate enhancements of $\approx 10^5$ over thermal controls. The relative sonocatalytic and photocatalytic activities of these carbonyls are in general accord. A variety of terminal alkenes can be sonocatalytically isomerized. Increasing steric hindrance, however, significantly diminishes the observed rates. Alkenes without β-hydrogens will not serve as substrates.

The exact nature of the catalytic species generated during sonolysis remains unknown. Results are consistent with the generally accepted mechanism for alkene isomerization in analogous thermal(36) and photochemical systems (37),(38). This involves the formation of a hydrido-π-allyl intermediate and alkene rearrangement via hydride migration to form the thermodynamically more stable 2-alkene complex, as shown in a general sense in Equations 10-14. In keeping with this scheme, ultrasonic irradiation of $Fe(CO)_5$ in the presence of 1-pentene and CO does produce $Fe(CO)_4$(pentene), as determined by FTIR spectral stripping (27).

$$M(CO)_n \quad -)-)-) \blacktriangleright M(CO)_m + n-m \ CO \qquad [10]$$

$$M(CO)_m + 1\text{-alkene} \longrightarrow M(CO)_x(1\text{-alkene}) + m-x \ CO \qquad [11]$$

$$M(CO)_x(1\text{-alkene}) \longrightarrow M(CO)_x(H)(\pi\text{-allyl}) \qquad [12]$$

$$M(CO)_x(H)(\pi\text{-allyl}) \longrightarrow M(CO)_x(2\text{-alkene}) \qquad [13]$$

$$M(CO)_x(2\text{-ene}) + 1\text{-alkene} \longrightarrow M(CO)_x(1\text{-ene}) + 2\text{-alkene} \qquad [14]$$

Recently, we have demonstrated another sort of homogeneous sonocatalysis in the sonochemical oxidation of alkenes by O_2. Upon sonication of alkenes under O_2 in the presence of $Mo(CO)_6$, 1-enols and epoxides are formed in one to one ratios. Radical trapping and kinetic studies suggest a mechanism involving initial allylic C-H bond cleavage (caused by the cavitational collapse), and subsequent well-known autoxidation and epoxidation steps. The following scheme is consistent with our observations. In the case of alkene isomerization, it is the catalyst which is being sonochemical activated. In the case of alkene oxidation, however, it is the substrate which is activated.

$$\text{/\!\!\diagup\diagdown} \quad \text{-)-)-)} \blacktriangleright \quad \text{/\!\!\diagup\diagdown} \quad + \text{ H}^\bullet \qquad [15]$$

$$\text{/\!\!\diagup\diagdown} \quad + \text{ O}_2 \quad \longrightarrow \quad \text{/\!\!\diagup\diagdown O}_2{}^\bullet \qquad [16]$$

$$\text{/\!\!\diagup\diagdown O}_2{}^\bullet + \text{/\!\!\diagup\diagdown} \quad \longrightarrow \quad \text{/\!\!\diagup\diagdown O}_2\text{H} + \text{/\!\!\diagup\diagdown} \qquad [17]$$

$$\text{/\!\!\diagup\diagdown O}_2\text{H} + \text{/\!\!\diagup\diagdown} \quad \xrightarrow{\text{Mo(CO)}_6} \quad \text{/\!\!\diagup\diagdown OH} + \text{ O} \qquad [18]$$

Heterogeneous Systems

Liquid-Liquid Reactions. One of the major industrial applications of ultrasound is emulsification. The first reported and most studied liquid-liquid heterogeneous systems have involved ultrasonically dispersed mercury. The use of such emulsions for chemical purposes was delineated by the extensive investigations of Fry and coworkers, (39),(40),(41) who have reported the sonochemical reaction of various nucleophiles with α,α'-dibromoketones and mercury. There are significant synthetic advantages to the use of ultrasound in these systems. For example, such Hg dispersions will react even with quite sterically hindered ketones, yet will introduce only one nucleophilic group even in sterically undemanding systems. Fry believes that the effect of the ultrasound in this system is a kinetic rate enhancement, presumably due to the large surface area of Hg generated in the emulsion.

Liquid-Solid Reactions. The effects of ultrasound on liquid-solid heterogeneous organometallic reactions has been a matter of intense recent investigation. The first use of ultrasound to prepare organo-metallic complexes of the main group metals (e.g. lithium, magnesium, and aluminum) from organic halides, however, originates in the often overlooked work of Renaud (42). The report by Luche in 1980 of the use of an ultrasonic cleaner to accelerate lithiation reactions(43) initiated much of the recent interest (44). Various groups, including Boudjouk's (45) and Ishikawa's (46), have dealt with extremely reactive metals, such as Li, Mg, or Zn, as stoichiometric reagents for a variety of common transformations. The specific origin of the rate and yield improvements has not yet been established in these systems. Ultrasonic cleaning of the reactive metal surface to remove passivating impurities (e.g. water, hydroxide, metal halide, or organolithium) are likely to be important (47).
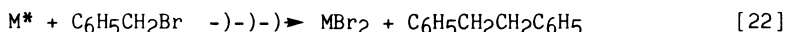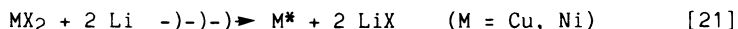   The activation of less reactive metals continues to attract major efforts in heterogeneous catalysis, metal-vapor chemistry, and synthetic organometallic efforts. Given the extreme conditions generated by acoustic cavitation at surfaces, analogies to autoclave conditions or to metal-vapor reactors may be appropriate.   In order to probe the potential generality of ultrasonic activation of hetero-geneous reactions, we examined (48) 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, (49) the formation of the early transition metal carbonyls still require "bomb" conditions (100-300 atm of CO, 100-300°C) and are prepared in only

moderate yields (50). 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 tetrahydrofuran or diglyme solutions of transition metal halides with Na sand in the presence of ultrasound gave fair to good yields of the carbonyl anions for V, Nb, Ta, Cr, Mo, W, Mn, Fe, and Ni, even at 10° and 1 atm. CO. Solubility of the metal halide is necessary for effective reaction. An ultrasonic cleaning bath was found to be of only marginal use when compared to the higher intensity immersion horn. Since these reactions are run at low pressures, they may prove uniquely useful in the production of ^{13}CO labeled carbonyl complexes.

$$MCl_5 + Na + CO \ -)-)-) \rightarrow M(CO)_6^- \quad (M=V,Nb,Ta) \qquad [19]$$

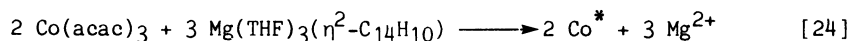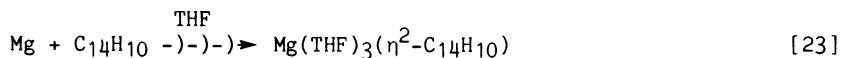$$MCl_6 + Na + CO \ -)-)-) \rightarrow M_2(CO)_{10}^{-2} \quad (M=Cr,Mo,W) \qquad [20]$$

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

The reduction of transition metal halides with Li has been recently extended by Boudjouk and coworkers for Ullman coupling (benzyl halide to bibenzyl) by Cu or Ni, using a low intensity cleaning bath (51). Ultrasound dramatically decreased the time required for complete reduction of the metal halides ($\approx$12 h without, <40 minutes with ultrasound). The subsequent reactivity of the Cu or Ni powders was also substantially enhanced by ultrasonic irradiation. This allowed significant increases in the yield of bibenzyl (especially for Ni) at lower temperatures, compared to simple stirring.

$$MX_2 + 2 \ Li \ -)-)-) \rightarrow M^* + 2 \ LiX \quad (M = Cu, Ni) \qquad [21]$$

$$M^* + C_6H_5CH_2Br \ -)-)-) \rightarrow MBr_2 + C_6H_5CH_2CH_2C_6H_5 \qquad [22]$$

Another recent application of ultrasound to the activation of transition metals was reported (52) by Bönnemann, Bogdavovic, and coworkers. An extremely reactive Mg species was used to reduce metal salts in the presence of cyclopentadiene, 1,5-cyclooctadiene, and other ligands to form their metal complexes. The reactive Mg species, characterized as Mg(THF)$_3$(anthracene), was produced from Mg powder in

tetrahydrofuran solutions containing a catalytic amount of anthracene
by use of an ultrasonic cleaning bath. A plausible scheme for this
reaction has been suggested:

$$Mg + C_{14}H_{10} \xrightarrow{\text{THF}} Mg(THF)_3(\eta^2\text{-}C_{14}H_{10}) \qquad [23]$$

$$2\ Co(acac)_3 + 3\ Mg(THF)_3(\eta^2\text{-}C_{14}H_{10}) \longrightarrow 2\ Co^* + 3\ Mg^{2+} \qquad [24]$$

$$2Co^* + 2C_5H_6 + 3\ 1,5\text{-}C_8H_{12} \longrightarrow 2Co(Cp)(COD) + C_8H_{14} \qquad [25]$$
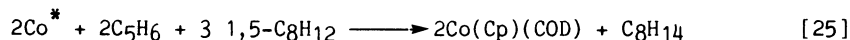
The effects of ultrasound on heterogeneous systems are quite
general, however, and ultrasonic rate enhancements for many non-
metallic insoluble reagents also occurs ($\underline{2}$). Ultrasound has been used
to enhance the rates of mass transport near electrode surfaces, and
thus to enhance rates of electrolysis. This has had some rather
useful synthetic applications for the production of both organic and
inorganic chalcogenides. The electrochemical reduction of insoluble
Se or Te powder by a carbon cloth electrode in the presence of low
intensity ultrasonic irradiation produces sequentially E_2^{-2} and E^{-2}
(where E is either Se or Te). With generally high current efficiency,
these species can be used in a variety of interesting reactions
including, for example, the synthesis of $Cp_2Ti(Se_5)$ from Cp_2TiCl_2.
Luche as reported the use of ultrasound to accelerate allylations of
organic carbonyls by Sn in aqueous media ($\underline{53}$). 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 reduc-
tion of $RuCl_3$ in the presence of 1,5-cyclooctadiene ($\underline{54}$). The use of
ultrasound with Zn is a likely area for routine use in the synthesis
and reduction of various organometallic complexes.

The intercalation of organic or inorganic compounds as guest
molecules into layered inorganic solid hosts permits the systematic
change of optical, electronic, and catalytic properties. The kinetics
of intercalation, however, are generally slow, and syntheses usually
require high temperatures and very long times. We have recently found
that high intensity ultrasound <u>dramatically</u> increases the rates of
intercalation (by as much as 200-fold) of a wide range of compounds
(including amines, metallocenes, and metal sulfur clusters) into
various layered inorganic solids (such as ZrS_2, V_2O_5, TaS_2, MoS_2, and
MoO_3) ($\underline{55}$). Scanning electron microscopy of the layered solids
suggests the origin of our observed rate enhancements. After sonica-
tion, in the presence or absence of guest compounds, a significant
decrease in the particle size of the host solid occurs. Starting with
solids of 60 to 90 μm diameters, after 10 m. sonication the particle
size is 5 to 10 μm. Upon further sonication, particle size does <u>not</u>
change; the extent of surface damage, however, continues to increase
substantially over the next several hours. Both the increase in
surface area and the effects of surface damage appear to be important
factors in the enhancement of intercalation ($\underline{56}$).

<u>Applications to Heterogeneous Catalysis.</u> 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 (57).

However, ultrasonic rate enhancements of heterogeneous catalysis
have usually been relatively modest (less than tenfold).   The effect
of irradiating operating catalysts is often simply due to improved
mass transport (58).   In addition, increased dispersion during the
formation of catalysts under ultrasound (59) will enhance reactivity,
as will the fracture of friable solids (e.g., noble metals on C or
silica (60),(61),(62) or malleable metals (63)).

We have recently discovered that hydrogenation of alkenes by Ni
powder is dramatically enhanced ($>10^5$-fold) by ultrasonic irradiation
(64).   After sonication of Ni powders under H_2 or Ar, the rapid
hydrogenation of alkene solutions occurs even at 25° and 1 atm. of H_2;
without sonication, no detectable hydrogenation occurs. This is not a
simple surface area effect, since we start with 5 μm sized particles
and they do not decrease in size significantly even after lengthy
irradiation (as determined by both SEM and BET surface area
measurements).   There is, however, a very interesting change in
surface morphology, as shown in Figure 4, which smooths the initially
crystalline surface.   In addition, the aggregation of particles
increases dramatically upon ultrasonic irradiation, as shown in Figure
5.   We have used Auger electron spectroscopy to provide a depth
profile of the surface's elemental analysis. The effect of ultrasonic
irradiation is to thin substantially the passivating oxide coating to
which Ni is quite prone.   It appears likely that the changes in
surface morphology, in the degree of aggregation, and in the surface's
elemental composition originate from inter-particle collisions caused
by the turbulent flow and shock waves created by high intensity
ultrasound.   Previous work on bulk Fe showed similar removal of a
passivating layer upon ultrasonic irradiation (65).

Concluding Remarks

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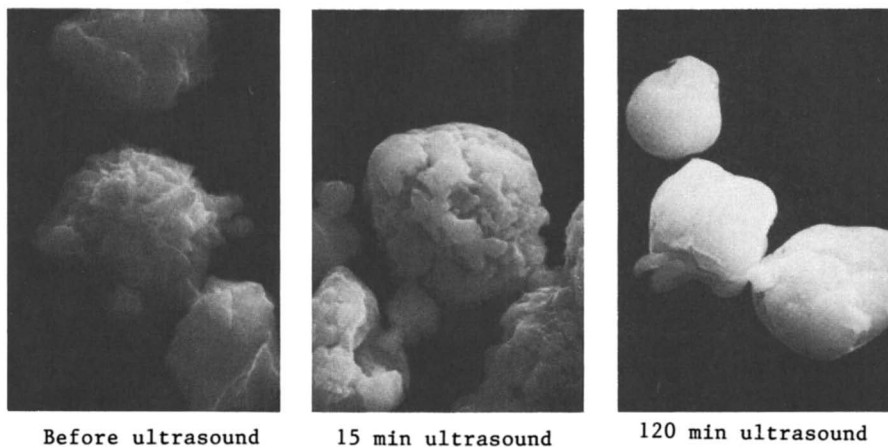useful guides in this exploration.

Before ultrasound   15 min ultrasound   120 min ultrasound

Figure 4. The effect of ultrasonic irradiation on surface
morphology of approximately 5 μm as shown by scanning electron
micrographs of Ni powder.

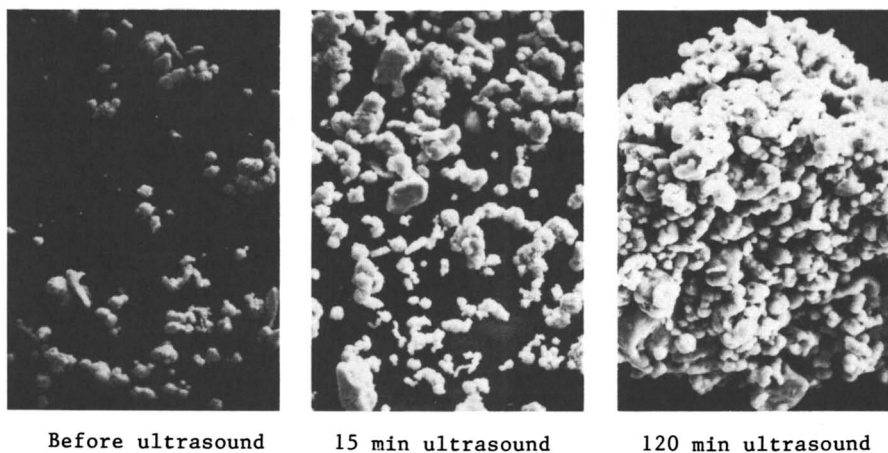Before ultrasound   15 min ultrasound   120 min ultrasound

Figure 5. The effect of ultrasonic irradiation on particle
aggregation as shown by scanning electron micrographs of Ni
powder (at 10 X less magnification than Figure 4).

Acknowledgments

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