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. Cavitation 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 acoustic cavitation. When sound passes through a
liquid, it consists of expansion (negative-pressure) waves and com­
pression (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 chemis­
try. To indicate ultrasonic irradiation ("sonication"), we will use
as our symbol: -)-)-
. Sonocatalysis will be restricted in its use
only to the creation of a catalytically competent intermediate by
ultrasonic irradiation; we will not refer to a simple sonochemical
rate enhancement of an already ongoing reaction by this term.

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 \(\approx1500\) m/sec, ultrasound has acoustic wavelengths of
roughly 7.5 to 0.015 \(\text{cm}\). 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 cavi­
tation in a homogeneous liquid should be considered separately from
cavitation near an interface.

The tensile strength of a pure liquid is determined by the attrac­
tive intermolecular forces which maintain its liquid state; the calcu­
lated tensile strength of water, for example, is in excess of \(-1000\)
atmospheres \(\text{atm}\) \(\text{of atm}\). 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 \(\approx5200^\circ\text{K}\) with
pressures of hundreds of atmospheres \(\text{atm}\) \(\text{of atm}\)!!

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 \(\text{Ellis}\) and Lauterborn \(\text{Lauterborn}\) (shown

In High-Energy Processes in Organometallic Chemistry; Suslick, K.;
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 ultrasonic cleaning (11). A second contribution to erosion created by cavitation involves the impact of shock waves generated by the implosive 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 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.

**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 applications, 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 atmosphere work (shown in Figure 2) and for moderate pressures (<10 atm.). These configurations may be used for both homogeneous and heterogeneous sonochemistry. Ultrasonic horns are available from several manufacturers (14) at modest cost and are used primarily by biochemists for cell disruption. A variety of sizes of power supplies and titanium horns are available, thus allowing flexibility in sample size. 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 sonochemistry 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

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

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 cavitation 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, 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 (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 (Y=Cp/Cv, 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 Fe2(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 cavitation 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.

\[
\text{Fe(CO)}_5 \rightarrow \text{Fe(CO)}_5(n=1-5) \quad [1]
\]
\[
\text{Fe(CO)}_3 + \text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_8 \quad [2]
\]
\[
2 \text{Fe(CO)}_4 \rightarrow \text{Fe}_2(\text{CO})_8 \quad [3]
\]
\[
\text{Fe}_2(\text{CO})_8 + \text{Fe(CO)}_5 \rightarrow \text{Fe}_3(\text{CO})_{12} + \text{CO} \quad [4]
\]

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$_4$H$_4$)$_2$(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)$_5$-nL$_n$, 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)$_4$L is not sonochemically converted to Fe(CO)$_3$L$_2$ on the time scale of its production from Fe(CO)$_5$. These observations are consistent with the same primary sonochemical event responsible for clusterification:
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 independent 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.

Initiation of Homogeneous Catalysis. 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 ≈10⁵ 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).

\[
M(CO)_n \rightarrow M(CO)_m + n-m \text{ CO} \tag{10}
\]
\[
M(CO)_m + 1-\text{alkene} \rightarrow M(CO)_x(1-\text{alkene}) + m-x \text{ CO} \tag{11}
\]
\[
M(CO)_x(1-\text{alkene}) \rightarrow M(CO)_x(H)(\pi-\text{allyl}) \tag{12}
\]
\[
M(CO)_x(H)(\pi-\text{allyl}) \rightarrow M(CO)_x(2-\text{alkene}) \tag{13}
\]
\[
M(CO)_x(2-\text{ene}) + 1-\text{alkene} \rightarrow M(CO)_x(1-\text{ene}) + 2-\text{alkene} \tag{14}
\]

Recently, we have demonstrated another sort of homogeneous sonocatalysis in the sonochemical oxidation of alkenes by O₂. Upon sonication of alkenes under O₂ 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 cavitation 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.
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 organometallic 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 heterogeneous 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. 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.

\[
MC_5 + Na + CO \rightarrow M(CO)_6^- \quad (M=V,Nb,Ta) \quad [19]
\]

\[
MC_6 + Na + CO \rightarrow M_2(CO)_{10}^- \quad (M=Cr,Mo,W) \quad [20]
\]

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 WC_16, 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}^- . 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 dibenzyl) by Cu or Ni, using a low intensity cleaning bath (51). Ultrasound dramatically decreased the time required for complete reduction of the metal halides (≈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 dibenzyl (especially for Ni) at lower temperatures, compared to simple stirring.

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

\[
M^* + C_6H_5CH_2Br \rightarrow MBr_2 + C_6H_5CH_2CH_2C_6H_5 \quad [22]
\]

Another recent application of ultrasound to the activation of transition metals was reported (52) by Bönneumann, 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:

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

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

\[ 2\text{Co}^* + 2\text{C}_5\text{H}_6 + 31,5-C_8\text{H}_{12} \rightarrow 2\text{Co(Cp)(COD)} + C_8\text{H}_{14} \quad [25] \]

The effects of ultrasound on heterogeneous systems are quite general, however, and ultrasonic rate enhancements for many non-metallic insoluble reagents also occurs (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$_2^-$ 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$_2$Ti(Se$_6$) from Cp$_2$TiCl$_2$. Luche as reported the use of ultrasound to accelerate allylations of organic carbonyls by Sn in aqueous media (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 reduction of RuCl$_3$ in the presence of 1,5-cyclooctadiene (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 dramatically increases the rates of intercalation (by as much as 200-fold) of a wide range of compounds (including amines, metalloccenes, and metal sulfur clusters) into various layered inorganic solids (such as ZrS$_2$, V$_2$O$_5$, TaS$_2$, MoS$_2$, and MoO$_3$) (55). Scanning electron microscopy of the layered solids suggests the origin of our observed rate enhancements. After sonication, 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 not 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 (56).

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 (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 (>105-fold) by ultrasonic irradiation (64). After sonication of Ni powders under H2 or Ar, the rapid hydrogenation of alkene solutions occurs even at 25° and 1 atm. of H2; 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 generation of organometallic species as synthetic intermediates will continue to find application in nearly any case where interphase mixing is a problem. Much less explored, but potentially quite exciting, is the use of sonochemistry to create high-energy chemistry in condensed phases at room temperature. Unique examples of sonochemical reactivity quite different from thermal or photochemical processes have been noted. The analogies to shock-wave and gas-phase pyrolyses, to "bomb" reactions, and to metal vapor chemistry may prove useful guides in this exploration.
Figure 4. The effect of ultrasonic irradiation on surface morphology of approximately 5 μm as shown by scanning electron micrographs of Ni powder.

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).
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