# Sonochemistry

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**Ultrasound causes high-energy chemistry. It does so through the process of acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. During cavitational collapse, intense heating of the bubbles occurs. These localized hot spots have temperatures of roughly 5000°C, pressures of about 500 atmospheres, and lifetimes of a few microseconds. Shock waves from cavitation in liquid-solid slurries produce high-velocity interparticle collisions, the impact of which is sufficient to melt most metals. Applications to chemical reactions exist in both homogeneous liquids and in liquid-solid systems. Of special synthetic use is the ability of ultrasound to create clean, highly reactive surfaces on metals. Ultrasound has also found important uses for initiation or enhancement of catalytic reactions, in both homogeneous and heterogeneous cases.**

IN A GENERAL SENSE, CHEMISTRY IS THE STUDY OF THE interaction of energy and matter. Chemical reactions require energy, in one form or another, to proceed: chemistry stops as the temperature approaches absolute zero. One has only limited control, however, over the nature of this interaction. In large part, the properties of a specific energy source determines the course of a chemical reaction. Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule, as shown in Fig. 1. Ultrasound is a unique means of interacting energy and matter.

The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, sonochemistry derives principally from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation serves as a means of concentrating the diffuse energy of sound. It is the underlying phenomenon responsible for sonochemistry and sonoluminescence. Bubble collapse induced by cavitation produces intense local heating, high pressures, and very short lifetimes (*1*). These hot spots have temperatures of roughly 5000°C, pressures of about 500 atmospheres, and heating and cooling rates greater than $10^9$ K/s. For perspective, within the liquid irradiated by an inexpensive, table-top ultrasonic apparatus, one can create the temperature of the sun's surface, the pressure of deep oceanic trenches, and the cooling rate of molten metal splatted onto a liquid-helium–cooled surface!

Related phenomena occur with cavitation in liquid-solid systems. Near an extended solid surface, cavity collapse is nonspherical and drives high-speed jets of liquid into the surface. This process can produce newly exposed, highly heated surfaces. In contrast, during ultrasonic irradiation of liquid-powder slurries, cavitation and the shock waves it creates can accelerate solid particles to high velocities. The resultant interparticle collisions are capable of inducing dramatic changes in surface morphology, composition, and reactivity.

The chemical effects of ultrasound are diverse and include dramatic improvements in both stoichiometric and catalytic reactions (*2–5*). In some cases, ultrasonic irradiation can increase reactivities by nearly a millionfold. Investigations into the chemical effects of ultrasound during the past few years can be delineated in three areas: homogeneous sonochemistry, heterogeneous sonochemistry, and sonocatalysis (which overlaps the first two). In each area, fundamental new discoveries of unusual chemical reactivities have been made, and substantial progress in our understanding of the responsible phenomena has been accomplished (*5, 6*).

## Acoustic Cavitation in Homogeneous Liquids

The velocity of sound in liquids is typically ~1500 m/s; ultrasound spans the frequencies of roughly 15 kHz to 10 MHz, with associated acoustic wavelengths of 10 to 0.01 cm. These are obviously not molecular dimensions. 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 nonlinear acoustic process for sonochemistry is cavitation. Its initial observation was in 1895 during speed trials of the first modern destroyer, the H.M.S. *Daring*; bubble formation, severe vibration, and surface damage to the propellers were reported (*7*). In attempting to explain such observations (as well as the origin of tea kettle noise, a related phenomenon), Lord Rayleigh described (*8*) the first mathematical model for the collapse of cavities in incompressible liquids and predicted enormous local temperatures (10,000 K) and pressure (10,000 atm) during such collapse. Ten years later, Richards and Loomis reported the first chemical and biological effects of ultrasound (*9*).

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 the local environment. Cavity collapse in a homogeneous liquid is very different from cavitation near a liquid-solid interface, which will be considered later.

Formation of cavities in liquids is a nucleated process. The theoretical tensile strength of a pure liquid is so great as to preclude cavity formation simply from the negative pressure of an acoustic expansion wave under typical laboratory conditions. Instead, nucleation of bubbles occurs at weak points in the liquid, such as gas-filled crevices in suspended particulate matter or from transient microbubbles from prior cavitation events.

Bubble growth in an irradiated liquid can occur through several

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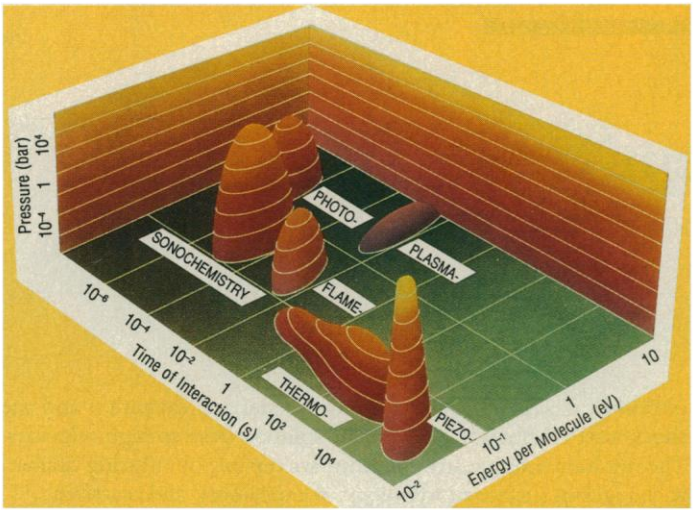

**Fig. 1.** Chemistry: the interaction of energy and matter. The three axes represent duration of the interaction, pressure, and energy per molecule. [Reprinted from (*6*) with permission © *Scientific American*]

different mechanisms. With high-intensity ultrasound, a small cavity may grow rapidly through inertial effects. If its rate of expansion is sufficiently rapid, it will not have time to recompress during the positive-pressure half of the acoustic cycle. At lower acoustic intensities, slow cavity growth can also occur. This process is called rectified diffusion and arises because the cavity's surface area is slightly greater during expansion than during compression; therefore, growth processes are slightly faster than shrinking processes. Thus, over many acoustic cycles, the cavity will grow.

At some point, the cavity can reach a resonant size where it can efficiently absorb energy from the sound field. This size is determined by the frequency of the ultrasound. At 20 kHz, the critical size is ~170 μm in diameter. Such a cavity, if it is in phase with the sound field, can then grow rapidly in the course of a single expansion cycle. Once the cavity has overgrown, it can no longer efficiently absorb energy from the sound field and can no longer sustain itself. The surrounding liquid rushes in and the cavity implodes.

Compression of a gas generates heat. When the compression of cavities occurs in irradiated liquids, the collapse is more rapid than thermal transport. Thus one generates a short-lived, localized hot spot in an otherwise cold liquid. This hot spot is the source of homogeneous sonochemistry. Alternative mechanisms involving electrical microdischarge have been proposed (*10, 11*), but are generally out of favor; in many cases, they do not appear consistent with observed sonochemical reactions (*12, 13*).

The enormous local temperatures and pressures and the extraordinary heating and cooling rates (*1*) generated by cavitational collapse mean that ultrasound provides an unusual mechanism for generating high-energy chemistry. Like photochemistry, very large amounts of energy are introduced in a short-period of time, but it is thermal, not electronic, excitation. As in flash pyrolysis, high thermal temperatures are reached, but the duration is very much shorter (by ~$10^4$) and the temperatures are even higher (by five- to tenfold). Similar to shock-tube chemistry or multiphoton infrared laser photolysis, cavitational heating is very short-lived, but occurs within condensed phases. Furthermore, sonochemistry has a high-pressure component, which suggests that one might be able to produce on a microscopic scale the same macroscopic conditions of high–temperature-pressure "bomb" reactions or explosive shock-wave synthesis in solids.

Control of sonochemical reactions is subject to the same limitation that any thermal process has: the Boltzmann energy distribution means that the energy per individual molecule will vary widely. One does have easy control, however, over the intensity of heating generated by acoustic cavitation through the use of various physical parameters (including thermal conductivity of dissolved gases, solvent vapor pressure inside the bubble, and ambient pressure) (*3*). In contrast, frequency is much less important, at least within the range where cavitation can occur (a few hertz to a few megahertz) (*14*).

High-intensity ultrasonic probes (50 to 500 W/cm$^2$) of the type used for biological cell disruption are the most reliable and effective source for laboratory-scale sonochemistry. A typical apparatus that permits easy control over ambient temperature and atmosphere is shown in Fig. 2. Lower acoustic intensities can often be used in liquid-solid heterogeneous systems because of the reduced liquid tensile strength at the liquid-solid interface. For such reactions, a common ultrasonic cleaning bath will therefore often suffice. The low intensity available in these devices (~1 W/cm$^2$), however, can prove limiting. In addition, the standing wave patterns in ultrasonic cleaners require accurate positioning of the reaction vessel. On the other hand, ultrasonic cleaning baths are easily accessible, relatively inexpensive, and usable on a moderately large scale. Finally, for larger scale irradiations, flow reactors with high ultrasonic intensities are commercially available in modular units of as much as 20 kW.

Interest in acoustic cavitation extends well beyond its chemical effects, and includes fluid mechanics, heat transport, measurements of liquid tensile strength, and superheating and boiling phenomena. Furthermore, since ultrasound is heavily used both for medical treatment (such as hyperthermia for cartilage traumas) and diagnosis (such as sonography of fetal development), the biological and chemical effects of ultrasound are of immediate importance to the health services community (*15*).

## The Sonochemical Hot Spot

Because of the transient nature of the cavitation event, direct measurements of the conditions generated during bubble collapse are unavailable. Chemical reactions themselves can be used to probe reaction conditions. The effective temperature of cavitational collapse can be determined by the use of competing unimolecular reactions whose rate dependencies on temperature have already been measured. Tsang developed this "comparative-rate chemical ther-

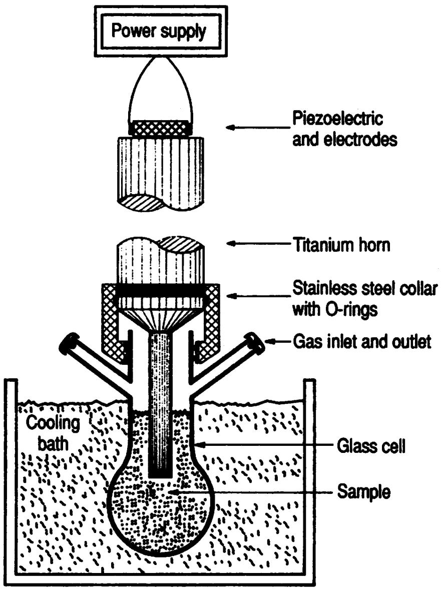

**Fig. 2.** A typical sonochemical apparatus. Ultrasound can be easily introduced into a chemical reaction with good control of temperature and ambient atmosphere. The usual piezoelectric ceramic is PZT, a lead zirconate titanate ceramic.

mometry" for gas-phase shock-tube studies (*16*), and Hammerton, Cline, and I extended its use to determine the effective temperature reached during cavitational collapse (*1*).

The sonochemical ligand substitutions of volatile metal carbonyls were used as these comparative rate probes (Eqs. 1 and 2, where the symbol $\xrightarrow{)))}$ represents ultrasonic irradiation of a solution). These reactions were chosen for multiple reasons: (i) the first step of these reactions is a unimolecular dissociation; (ii) the final products are easy to monitor; and (iii) the temperature dependence of these reactions had already been determined through gas-phase laser pyrolysis by Golden, Smith, and co-workers (*17*).

$$\mathrm{M(CO)}_x \xrightarrow{)))} \mathrm{M(CO)}_{x-n} + n\,\mathrm{CO} \tag{1}$$

where M = Fe, Cr, Mo, W

$$\mathrm{M(CO)}_{x-n} + n\,\mathrm{PR}_3 \rightarrow \mathrm{M(CO)}_{x-n}(\mathrm{PR}_3)_n \tag{2}$$

where R is an alkyl or aryl group.

Our group discovered that there were in fact *two* sonochemical reaction sites. The liquid-phase concentration of the dissolved metal carbonyl can be changed independently from its gas-phase concentration (its vapor pressure) by varying the ambient temperature. The rates of these reactions were monitored as a function of these separable concentrations, showing that one reaction site occurred in the bubble's gas phase and that the second took place in a phase that was initially a liquid. The latter presumably corresponds to a shell of liquid around the bubble heated after collapse.

In these kinetic studies, the relative sonochemical rates for Eq. 1 in both the gas-phase and initially liquid-phase reaction sites were determined. In combination with the known temperature behavior of these reactions, we could then determine the conditions present during cavitational collapse in both reaction zones. The effective temperature of these hot spots is in excess of 5000 K in the gas-phase reaction zone and ~2000 K in the initially liquid zone (*1*). Of course, the comparative rate data represent only a composite temperature: during the cavitational collapse, the temperature has a highly dynamic profile, as well as a spatial temperature gradient in the liquid surrounding the gas-phase hot spot. A more realistic view of the temporal and spatial evolution of the liquid-zone temperature may be obtained with a heat transport model calculated by an explicit method of finite differencing (*1*). This simple model includes only conductive heat transport and has *no* adjustable parameters; nonetheless, it agrees reasonably well with the data. The model also gives us a sense of scale concerning the liquid reaction zone. It extends only ~200 nm from the bubble surface and has an effective lifetime of less than 2 μs after collapse. The size of the heated shell corresponds to a reactive liquid layer ~500 molecules thick.

## Homogeneous Sonochemistry

The chemical effects of ultrasound on liquids have been studied for many years. Most of these studies, however, have dealt with the sonolysis of water. The primary products are $H_2$ and $H_2O_2$; other high-energy intermediates have been suggested, including $HO_2$, H·, OH·, and $e^-$(aq). The elegant work of Riesz and collaborators used electron paramagnetic resonance with chemical spin traps to demonstrate definitively the generation of H· and OH· during ultrasonic irradiation, even with clinical sources of ultrasound (*18*). The extensive recent work in Henglein's laboratory (*19*) involving aqueous sonochemistry of dissolved gases has established analogies to combustion processes. As one would expected, the sonolysis of water, which produces both strong reductants and oxidants, is capable of causing secondary oxidation and reduction reactions, as often observed by Margulis and co-workers (*11*).

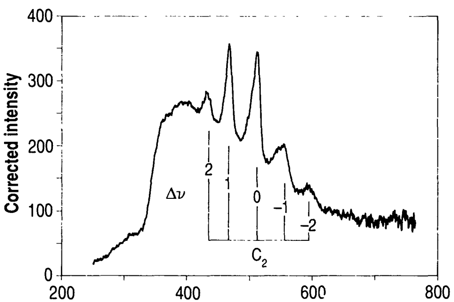

**Fig. 3.** Sonoluminescence of hydrocarbons. The sonoluminescence spectrum is dominated by emission from excited states of the diatomic molecule $C_2$. This spectrum is from dodecane under argon at 4°C. [Reprinted from (*13*) with permission © American Chemical Society]

The ultrasonic irradiation of organic liquids, however, has been little studied. My research group established that virtually all organic liquids will generate free radicals upon ultrasonic irradiation (*20, 21*), as long as the total vapor pressure is low enough to allow effective cavitational collapse. Wang in my laboratory found that the sonolysis of simple hydrocarbons (for example, *n*-alkanes) creates the same kinds of products associated with very high temperature pyrolysis. Most of these products ($H_2$, $CH_4$, and the smaller 1-alkenes) derive from a well-understood radical-chain mechanism. Sonolysis also produces large amounts of acetylene and propyne. In the limit of very high temperatures, acetylene is the most stable hydrocarbon (because of entropic considerations), hence its production during sonolysis.

The sonochemistry of solutes dissolved in organic liquids also remains largely unexplored. The sonochemistry of metal carbonyl compounds is an exception. Detailed studies of these systems led to important mechanistic understandings of the nature of sonochemistry. A variety of unusual reactivity patterns have been observed during ultrasonic irradiation, including multiple ligand dissociation, novel metal-cluster formation, and the initiation of homogeneous catalysis (discussed below) at low ambient temperature, with rate enhancements greater than 100,000-fold (*22–24*).

In 1981, Schubert, Goodale, and I reported the first sonochemistry of discrete organometallic complexes and demonstrated the effects of ultrasound on metal carbonyls in alkane solutions (*22*). The transition metal carbonyls were chosen for these initial studies because their thermal and photochemical reactivities have been well characterized and because the reaction mechanisms are relatively simple. The comparison among the thermal, photochemical, and sonochemical reactions of $Fe(CO)_5$ provides an excellent example of the unusual chemistry which acoustic cavitation can induce.

Thermolysis of $Fe(CO)_5$ gives pyrophoric, finely divided iron powder; ultraviolet photolysis yields $Fe_2(CO)_9$, through the intermediate $Fe(CO)_4$; multiphoton infrared photolysis in the gas phase yields isolated Fe atoms. Multiple ligand dissociation [generating $Fe(CO)_3$, $Fe(CO)_2$, and so forth] is not available from ordinary thermal or photochemical processes, but can occur in matrix-isolated and gas-phase laser photolyses. These observations reflect the dual difficulties inherent in high-energy chemistry: first, to deliver sufficient energy in a usable form, and second, to quench the highly energetic intermediates before complete decomposition occurs.

Sonolysis of $Fe(CO)_5$ in alkane solvents in the absence of alternative ligands causes the unusual clusterification to $Fe_3(CO)_{12}$ (*23*). The rate of decomposition is cleanly first order, and the logarithm of the observed first-order rate coefficient is linear with the solvent vapor pressure, consistent with a simple dissociation process activated by the intense local heating of acoustic cavitation. The proposed chemical mechanism by which $Fe_3(CO)_{12}$ is formed during the sonolysis of $Fe(CO)_5$ is shown in Eqs. 3 through 6.

$$Fe(CO)_5 \xrightarrow{)))} Fe(CO)_x + (5 - x)CO \qquad (x = 0\text{–}4) \tag{3}$$

$$Fe(CO)_3 + Fe(CO)_5 \rightarrow Fe_2(CO)_8 \tag{4}$$

$$2Fe(CO)_4 \rightarrow Fe_2(CO)_8 \tag{5}$$

$$Fe_2(CO)_8 + Fe(CO)_5 \rightarrow Fe_3(CO)_{12} + CO \tag{6}$$

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 (abbreviated L) produces $Fe(CO)_{5-n}L_n$, $n = 1, 2$, and 3. Kinetic studies are consistent with the same primary sonochemical event responsible for clusterification.

## Sonoluminescence

Ultrasonic irradiation of liquids can also produce light. This phenomenon, known as sonoluminescence, was first observed from water in 1934 by Frenzel and Schultes (*25*). As with sonochemistry, sonoluminescence derives from acoustic cavitation. Although sonoluminescence from aqueous solutions has been studied in some detail, only recently has significant work with non-aqueous liquids been reported.

The sonoluminescence spectrum of water consists of a peak at 310 nm and a broad continuum throughout the visible. An intensive study of aqueous sonoluminescence was conducted by Verrall and Sehgal (*26*). The emission at 310 nm is from excited state $OH\cdot$, but the continuum is difficult to interpret. Specific portions of this continuum are selectively quenched upon addition of nitric acid, which demonstrates that the continuum is from chemical species and not blackbody emission. Sonoluminescence from solutions of metal salts is characterized by atomic emission from the initially liquid-phase reaction zone (*27*) and has been seen from salt solutions of Li, Na, K, Rb, Ca, Sr, Ba, and Cu.

Quite recently, Flint and I reported the first sonoluminescence spectra of organic liquids (*13, 28*). With either alkanes or arenes, the observed emission is from excited states of $C_2(d^3\Pi_g - a^3\Pi_u$, the Swan lines), the same emission seen in flames (Fig. 3). The total intensity of the luminescence is strongly dependent on the solvent vapor pressure, which indicates that $C_2^*$ is formed from cavitational collapse. Consistent with these results, $C_2H_2$ is a major chemical product observed in the sonolysis of alkanes (*21*).

This observation of $C_2^*$ emission from alkanes and arenes under argon clearly demonstrates the similarity between flame chemistry and sonochemistry. Furthermore, the ultrasonic irradiation of alkanes in the presence of $N_2$ (or $NH_3$ or amines) gives emission from $CN^*$, but not from $N_2^*$. Emission from $N_2^*$ would have been expected if the sonoluminescence originated from microdischarge, whereas $CN^*$ emission is typically observed from thermal sources. When oxygen is present, emission from excited states of $CO_2$, CH, and OH is observed, as from flames.

For both aqueous and non-aqueous liquids, sonoluminescence is caused by chemical reactions of high-energy species formed during cavitational collapse. Its principal source is *not* blackbody radiation or electrical discharge. Sonoluminescence is a form of chemiluminescence.

## Ultrasound in Liquid-Solid Systems

Cavitation near extended liquid-solid interfaces is very different from cavitation in pure liquids. There are two proposed mechanisms for the effects of cavitation near surfaces: microjet impact and shock-wave damage. The asymmetry of the environment near the interface induces a deformation of the cavity during its collapse. This deformation is self-reinforcing, and it sends a fast-moving stream of liquid through the cavity at the surface with velocities greater than 100 m/s. This microjet impact has been observed by Lauterborn and co-workers in high-speed microcinemagraphic sequences (*29*), as shown in Fig. 4, and by flash microphotography by Crum (*30*), among others. Such impacts leave behind characteristic microscopic pitting in the surface. The second mechanism of cavitation-induced surface damage invokes shock waves created by cavity collapse in the liquid. The existence of both mechanisms has been established, but their relative importance is a matter of debate and probably depends on the method by which cavitation is produced.

The impingement of microjets and shock waves on the surface creates the localized erosion responsible for ultrasonic cleaning and many of the sonochemical effects on heterogeneous reactions. The cavitational erosion of metals generates newly exposed, highly

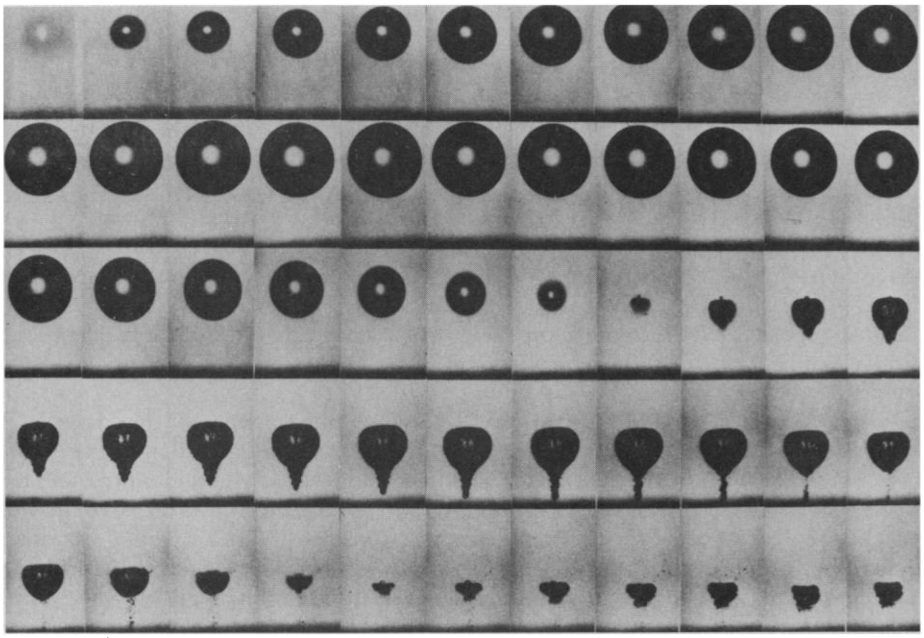

**Fig. 4.** Cavitation near a liquid-solid interface. High-speed microcinemagraphic sequence of laser-induced cavitation near a solid surface, showing the formation of a microjet impact; 75,000 frames per second. [Photograph courtesy of W. Lauterborn; reprinted from (*29*) with permission © Annual Reviews]

heated surfaces and ejects metal (in unknown form, perhaps as atoms or small clusters) from the surface. The importance of this process to corrosion and erosion phenomena of metals and machinery has been thoroughly reviewed elsewhere (*31*).

Microjet distortions of bubble collapse depend on a surface several times larger than the resonant bubble size. Thus, for solid particles smaller than ~200 μm, jet formation cannot occur with ultrasonic frequencies of ~20 kHz. In these cases, however, the shock waves created by homogeneous cavitation can create high-velocity interparticle collisions. My research group has found that the turbulent flow and shock waves produced by intense ultrasound can drive metal particles together at sufficiently high speeds to induce effective melting at the point of collision (*32*).

In order to better understand the nature of such interparticle collisions, Doktycz and I recently examined a series of transition metals as probes of the maximum temperatures and speeds reached during interparticle collisions (*32*). Using the irradiation of Cr, Mo, and W powders in decane at 20 kHz and 50 W/cm$^2$, one observes agglomeration and what appears to be localized melting for the first two metals, but not the third. On the basis of the melting points of these metals (1857°, 2617°, and 3410°C, respectively), the effective transient temperature reached at the point of impact during interparticle collisions is roughly 3000°C. From the volume of the melted region at the point of impact, we estimated the amount of energy generated during collision. From this, a lower estimate of the velocity of impact is roughly one half the speed of sound!

## Heterogeneous Sonochemistry

The use of high-intensity ultrasound to enhance the reactivity of metals as stoichiometric reagents has become a routine synthetic technique for many heterogeneous organic and organometallic reactions (*2–5, 33, 34*), especially those involving reactive metals, such as Mg, Li, or Zn. This development originated from the early work of Renaud and the more recent breakthroughs of Luche (*35*). The effects are quite general and apply to reactive inorganic salts and to main group reagents as well. Rate enhancements of more than tenfold are common, yields are often substantially improved, and by-products avoided. A few of the many examples of the sonochemistry of reactive reagents are shown in Eqs. 7 through 13, taken from the work of Luche, Boudjouk, Ishikawa, Mason, Ando, and Chou, among others, as well as our own (*2–5, 33–35*).

$$C_6H_5Br + Li \xrightarrow{)))} C_6H_5Li + LiBr \qquad (7)$$

$$RBr + Li + R'_2NCHO \xrightarrow[2.\ H_2O]{1.\ )))} RCHO + R'_2NH \qquad (8)$$

$$RR'C{=}O + BrCH_2CO_2R'' + Zn \xrightarrow{)))} RR'C(OH)CH_2CO_2R'' + ZnBr \qquad (9)$$

$$2o\text{-}C_6H_4(NO_2)I + Cu \xrightarrow{)))} o\text{-}(O_2N)H_4C_6\text{–}C_6H_4(NO_2) + 2CuI \qquad (10)$$

$$RR'HC\text{–}OH + KMnO_4(s) \xrightarrow{)))} RR'C{=}O \qquad (11)$$

$$C_6H_5CH_2Br + KCN \xrightarrow[Al_2O_3]{)))} C_6H_5CH_2CN \qquad (12)$$

$$(C_6H_5)_3P + Li \xrightarrow{)))} [(C_6H_5)_2PLi] \xrightarrow[2.\ CH_3I]{1.\ t\text{-}C_4H_9Cl} (C_6H_5)_2P(CH_3) \qquad (13)$$

Much less work has been done on the activation of less reactive metals. This goal continues to attract major efforts in both synthetic organometallic chemistry and heterogeneous catalysis. Given the extreme conditions generated by acoustic cavitation, analogies to autoclave conditions and to metal-vapor reactors may be appropriate. And in fact, ultrasound can be used at room temperature and pressure to promote heterogeneous reactions which normally occur only under extreme conditions of hundreds of atmospheres and hundreds of degrees.

In order to probe the generality of ultrasonic activation of heterogeneous reactions, Johnson and I examined some of the most difficult reactions known for transition metals: the attack of carbon monoxide on the very unreactive early transition metals (*36*). Even with the use of highly dispersed, very reactive transition metal slurries [as investigated by Rieke (*37*) and others], the formation of the early transition metal carbonyls still requires extreme conditions (in many cases, 100 to 300 atm of CO at 100° to 300°C) and gives 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 transition metal halides in tetrahydrofuran or diglyme with Na sand in the presence of ultrasound gave good yields of the carbonyl anions for V, Nb, Ta, Cr, Mo, W, Mn, Fe, and Ni, at 10°C and 1 atm of CO (Eqs. 14 and 15). Spectroscopic examination of this process revealed that the reduction process was sequential: reactive species that formed upon partial reduction were trapped by CO. Other recent reports (*38, 39*) have begun to reveal the generality of this approach to the synthesis of reactive transition metal powders.

$$MCl_5 + Na + CO \xrightarrow{)))} M(CO)_6^{-} \qquad (M = V, Nb, Ta) \qquad (14)$$

$$MCl_6 + Na + CO \xrightarrow{)))} M_2(CO)_{10}^{2-} \qquad (M = Cr, Mo, W) \qquad (15)$$

In collaboration with Green and his students at Oxford University, we recently examined another application of sonochemistry to difficult heterogeneous systems: the process of molecular intercalation (*40*). The adsorption of organic or inorganic compounds as guest molecules between the atomic sheets of layered inorganic solid hosts permits the systematic change of optical, electronic, and catalytic properties. Such materials have many technological applications (for example, lithium batteries, hydrodesulfurization catalysts, and solid lubricants). The kinetics of intercalation, however, are generally extremely slow, and syntheses usually require high temperatures and very long reaction times. High-intensity ultrasound dramatically 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 $MoO_3$). Scanning electron microscopy of the layered solids coupled to chemical kinetics studies demonstrated that the origin of the observed rate enhancements comes from particle fragmentation (which dramatically increases surface areas) and to a lesser extent from surface damage. The ability of high-intensity ultrasound to rapidly form uniform dispersions of micrometer-sized powders of brittle materials had not been previously recognized. The activation of heterogeneous reagents, especially nonmetals, often may be due to this effect.

In spite of the extensive application of ultrasound to chemical synthesis, the mechanism of rate enhancements in both stoichiometric and catalytic reactions of metals remained largely unexplored. The protocol used in my research group to examine heterogeneous sonochemistry and sonocatalysis has relied on a triptych of methodologies: (i) monitoring the effect of ultrasonic irradiation on the kinetics of the chemical reactivity of the solids, (ii) determining effects of irradiation on surface morphology and size distributions of powders and solids, and (iii) determining surface composition depth profiles. The power of this three-pronged approach has been proved in studies of the sonochemistry of transition metal powders (*41–43*).

Ultrasonic irradiation of liquids containing Cr, Mo, Ni, Cu, or Zn powders leads to dramatic changes in morphology (*32, 41–43*). The

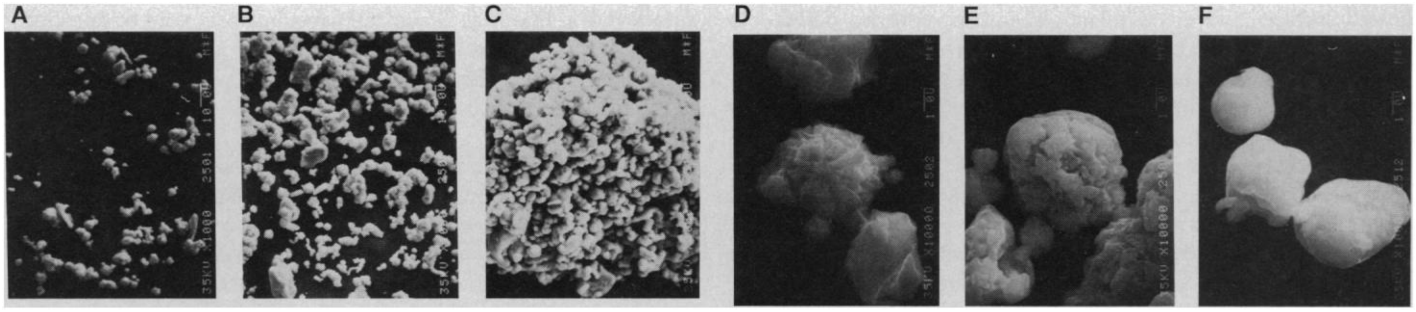

**Fig. 5.** The effect of ultrasonic irradiation on the particle agglomeration and surface morphology of Ni powder. High-velocity interparticle collisions caused by ultrasonic irradiation of slurries responsible for these effects. Note the magnification of the upper scanning electron micrographs is tenfold less than in the lower ones. (**A**) and (**D**) are before irradiation, (**B**) and (**E**) after 15-min irradiation, (**C**) and (**F**) after 120-min irradiation. [Reprinted from (*36*) with permission © American Chemical Society]

high-velocity interparticle collisions produced in such slurries cause smoothing of individual particles and agglomeration of particles into extended aggregates (Fig. 5). Surface composition was probed by Auger electron spectroscopy and sputtered neutral mass spectrometry to generate elemental depth profiles of these powders, which revealed that ultrasonic irradiation effectively removed the surface oxide coating (Fig. 6). The removal of such passivating coatings can dramatically improve reaction rates. For example, ultrasonic irradiation increases the reactivity of Zn powder as a stoichiometric reagent in the Reformatsky reaction (Eq. 9) by more than 50-fold (Fig. 7).

## Sonocatalysis

Catalytic reactions are of enormous importance in both laboratory and industrial applications. Catalysts are generally divided into two types. If the catalyst is a molecular or ionic species dissolved in a liquid, then the system is "homogeneous"; if the catalyst is a solid, with the reactants either in a percolating liquid or gas, then it is "heterogeneous." In both cases, it is often a difficult problem either to activate the catalyst or to keep it active.

Ultrasound has potentially important applications in both homogeneous and heterogeneous catalytic systems. The inherent advantages of sonocatalysis include (i) the use of low ambient temperatures to preserve thermally sensitive substrates and to enhance selectivity; (ii) the ability to generate high-energy species difficult to obtain from photolysis or simple pyrolysis; and (iii) the mimicry of autoclave reaction conditions (that is, high temperatures and pressures) on a microscopic scale.

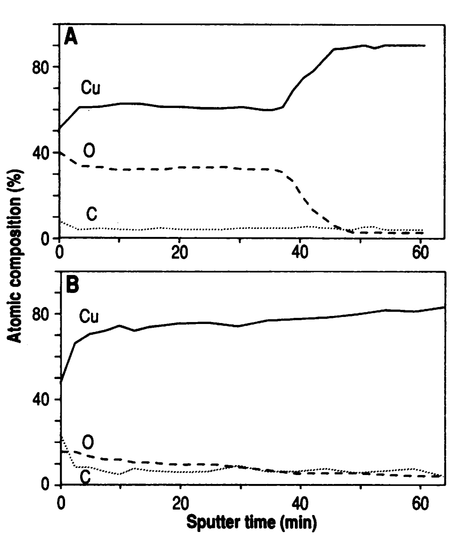

**Fig. 6.** Surface composition depth profiles of Cu powder (75-μm mean diameter) before and after ultrasonic irradiation. Depth profiles were derived from Auger electron spectra; sputtering times correspond to an erosion rate of ~270 Å/min. The upper depth profile is before ultrasonic irradiation; the lower after 4 hours of irradiation in dimethylformamide at 15°C. [Reprinted from (*43*) with permission © American Chemical Society]

Organometallic compounds are often used for homogeneous catalysis of various reactions. The starting organometallic compound, however, is often catalytically inactive until the loss of metal-bonded ligands (such as carbon monoxide) from the metal. Having demonstrated that ultrasound can induce ligand dissociation, the initiation of homogeneous catalysis by ultrasound becomes practical. The transient, coordinatively unsaturated species produced from the sonolysis of metal carbonyls are likely candidates, since Wrighton has shown that similar species produced photochemically are among the most active catalysts known (*44*).

A variety of metal carbonyls upon sonication will catalyze the isomerization of 1-alkenes to the internal alkenes. Initial turnover rates are as high as 100 moles of alkene isomerized per mole of precatalyst per hour, and represent rate enhancements of as much as $10^5$ 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.

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 and photochemical systems, which involves abstraction of a hydrogen atom by the metal to form a hydrido-π-allyl intermediate, followed by alkene rearrangement through hydride migration. This yields the thermodynamically more stable 2-alkene complex, which can then exchange with the excess 1-alkene in solution.

Heterogeneous catalysts are generally more industrially important than homogeneous systems. For example, virtually all of the petroleum industry is based on a series of catalytic transformations. Heterogeneous catalysts often require rare and expensive metals. The use of ultrasound offers some hope of activating less reactive, but also less costly, metals.

Some early investigations of the effects of ultrasound on heterogeneous catalysis can be found in the Soviet literature (*45*). In this early work, increases in turnover rates were usually observed upon ultrasonic irradiation, but were rarely more than tenfold. In the cases of modest rate increases, it appears likely that the cause is simply increased dispersion; this is especially important in the case of catalysts supported on brittle solids [such as noble metals on carbon (*46*)].

More impressive accelerations, however, have been recently reported, including hydrogenations (*41, 47, 48*) and hydrosilations (*46*) by Ni powder, Raney Ni, and Pd or Pt on carbon. In some of these reports, the origins of enhanced catalytic reactivity have been well defined (*41*). Such effects can occur in three distinct stages: (i) during the formation of supported catalysts, (ii) in the activation of preformed catalysts, or (iii) by the enhancement of catalytic behavior

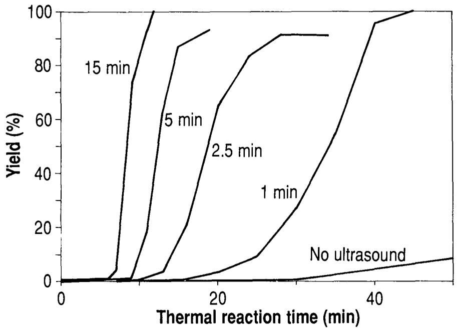

**Fig. 7.** Effect of ultrasound on Zn reactivity in a Reformatsky reaction (Eq. 9). Zinc powder (5-μm mean diameter) was irradiated in dioxane at 16°C for increasing lengths of time as indicated; reactants were then added, and products were monitored by gas chromatography–mass spectrometry. [Reprinted from (*42*) with permission © American Chemical Society]

during a catalytic reaction. Dramatic changes in surface morphology and composition lead to depassivation of the catalyst surface can cause large increases in activity; this is especially important in the case of metal powders (*41–43*).

For example, Casadonte recently discovered in my laboratory that hydrogenation of alkenes by Ni powder is enormously enhanced ($>10^5$-fold) by ultrasonic irradiation (*41*). The surface area did not change significantly even after lengthy irradiation. There is, however, a very interesting effect on the surface morphology (as shown in Fig. 5). Ultrasonic irradiation smooths, at a macroscopic scale, the initially crystalline surface and causes agglomeration of small particles. Both effects are probably due to interparticle collisions caused by cavitational shock waves. Auger electron spectroscopy reveals that there is a striking decrease in the thickness of the oxide coat after ultrasonic irradiation, just as in the case of stoichiometric reactions of Cu and Zn. The removal of this passivating layer is probably responsible for the $>10^5$-fold increase observed in catalytic activity.

## Conclusions and Future Directions

Chemical applications of ultrasound are just beginning to emerge. The very high temperatures and very short times of cavitational collapse makes sonochemistry a unique interaction of energy and matter. In addition, ultrasound is well suited to industrial applications. Since the reaction liquid itself carries the sound, there is no barrier to its use with large volumes. In fact, ultrasound is already heavily used industrially for the physical processing of liquids, such as emulsification, solvent degassing, solid dispersion, and sol formation. It is also extremely important in solids processing, including cutting, welding, cleaning, and precipitation.

The extension of ultrasound to the chemical processing of liquids is under way. The future uses of ultrasound to drive chemical reactions will be diverse. It is becoming a common tool in nearly any case where a liquid and a solid must react. In the synthesis of pharmaceuticals, for example, ultrasound may permit improved yields and facilitate reactions run on larger scale. In the development and use of catalysts, ultrasound is especially well suited. The ability of ultrasound to create highly reactive surfaces and thereby increase their catalytic activity has only just now been established. It is also likely that ultrasound can produce materials with unusual properties. The extraordinary temperatures and pressures reached during cavitational collapse, combined with the exceptionally high rates of cooling, may lead to the synthesis of novel solid phases difficult to prepare in other ways.

Studies of high-energy processes, such as sonochemistry, are important to the development of both the science of chemistry and new technologies. In its first recommendation, the Pimentel Report (*Opportunities in Chemistry*) proposed "an initiative to explore chemical reactions under conditions far removed from normal ambient conditions. Chemical behaviors under extreme pressures, extreme temperatures, . . . provide critical tests of our basic understandings of chemical reactions and new routes toward discovery of new materials and new devices" (*49*). Sonochemistry is in the midst of a renaissance, but remains in its infancy. Its potential impact on the scientific community is large and still developing.

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