

The Chemical Effects of Ultrasound

Intense ultrasonic waves traveling through liquids generate small cavities that enlarge and implode, creating tremendous heat. These extreme conditions provide an unusual chemical environment

by Kenneth S. Suslick

During the early tests of the first British destroyer in 1894, Sir John I. Thornycroft and Sydney W. Barnaby noticed a severe vibration from the destroyer's propeller. They suggested that large bubbles, or cavities, formed by the spinning propeller and imploded by water pressure, were the source of the vibrations. Thornycroft and Barnaby redesigned the propeller to reduce the vibrations from what came to be known as cavitation, but as the British navy built even faster propulsion systems the phenomenon became an increasingly significant problem. In 1917, therefore, the navy commissioned Lord Rayleigh to study the matter. He confirmed that the vibrations were due to the enormous turbulence, heat and pressure of imploding cavities. Although cavitation continues to be troublesome for nautical engineers, it has provided chemists with a unique environment for high-energy reactions.

Chemistry, after all, is the interaction of energy and matter. Specific energy sources limit the control chemists have over the reactivity of matter. Light interacts with matter on a short time scale at high energies, whereas

heat interacts on longer time scales at lower energies. The interaction of sound with matter through the process of cavitation makes available to chemists a range of energies on time scales that are not available from other sources.

Chemists usually induce cavitation not by applying mechanical pressure but rather by generating intense sound waves in a liquid. Such waves create alternating regions of compression and expansion that can form bubbles 100 microns in diameter. The bubbles implode violently in less than a microsecond, heating their contents to 5,500 degrees Celsius—about the temperature of the sun's surface.

The first chemist to recognize the unusual effects of intense sound waves traveling through a liquid, known as sonochemistry, was Alfred L. Loomis in 1927. In spite of his early results, the study of sonochemistry remained exceedingly modest. A renaissance in sonochemistry took place in the 1980's, soon after the advent of inexpensive and reliable generators of high-intensity ultrasound (sound pitched above human hearing at frequencies greater than 16 kilohertz, or 16,000 cycles per second).

Today ultrasound is applied in hospitals for medical imaging, in industry for welding plastics and cleaning materials and even in the home for burglar alarms and vaporizers. These applications, however, do not utilize the chemical effects of ultrasound. Ultrasound can increase the reactivity of metal powders by more than 100,000 times. Ultrasound can drive metal particles together at such high speeds that they melt at the point of collision, and ultrasound can generate microscopic flames in cold liquids.

These chemical effects of ultrasound arise from the physical processes that create, enlarge and implode gaseous and vaporous cavities in a liquid. Ultrasound waves, like all sound waves, consists of cycles of compression and expansion. Compression cycles exert a positive pressure on the liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another.

During the expansion cycle a sound wave of sufficient intensity can generate cavities. A liquid is held together by attractive forces, which determine the tensile strength of a liquid. In order for a cavity to form, a large negative pressure associated with the expansion cycle of the sound wave is needed to overcome the liquid's tensile strength.

The amount of negative pressure needed depends on the type and purity of the liquid. For truly pure liquids, tensile strengths are so great that available ultrasound generators cannot produce enough negative pressure to make cavities. In pure water, for instance, more than 1,000 atmospheres of negative pressure would be required, yet the most powerful ultrasound generators produce only about 50 atmospheres of negative pressure. The tensile strength of liquids is reduced, however, by gas trapped in the crevices of small solid particles. The effect is analogous to the reduction in strength that occurs from cracks in solid materials. When a gas-filled crevice is exposed to a negative-pressure cycle from a sound wave, the reduced pressure makes the gas in the crevice expand until a small bubble is released into solution. Most liquids are sufficiently contaminated by small particles to initiate cavitation. In tap

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water, negative pressures of only a few atmospheres will form bubbles.

A bubble in a liquid is inherently unstable. If the bubble is large, it will float away and burst at a surface; if it is small, it will redissolve into the liquid. A bubble irradiated with ultrasound, however, continually absorbs energy from alternating compression and expansion cycles of the sound wave. These cause the bubbles to grow and contract, striking a dynamic balance between the vapor inside the bubble and the liquid outside. In some cases the ultrasonic waves will sustain a bubble that simply oscillates in size.

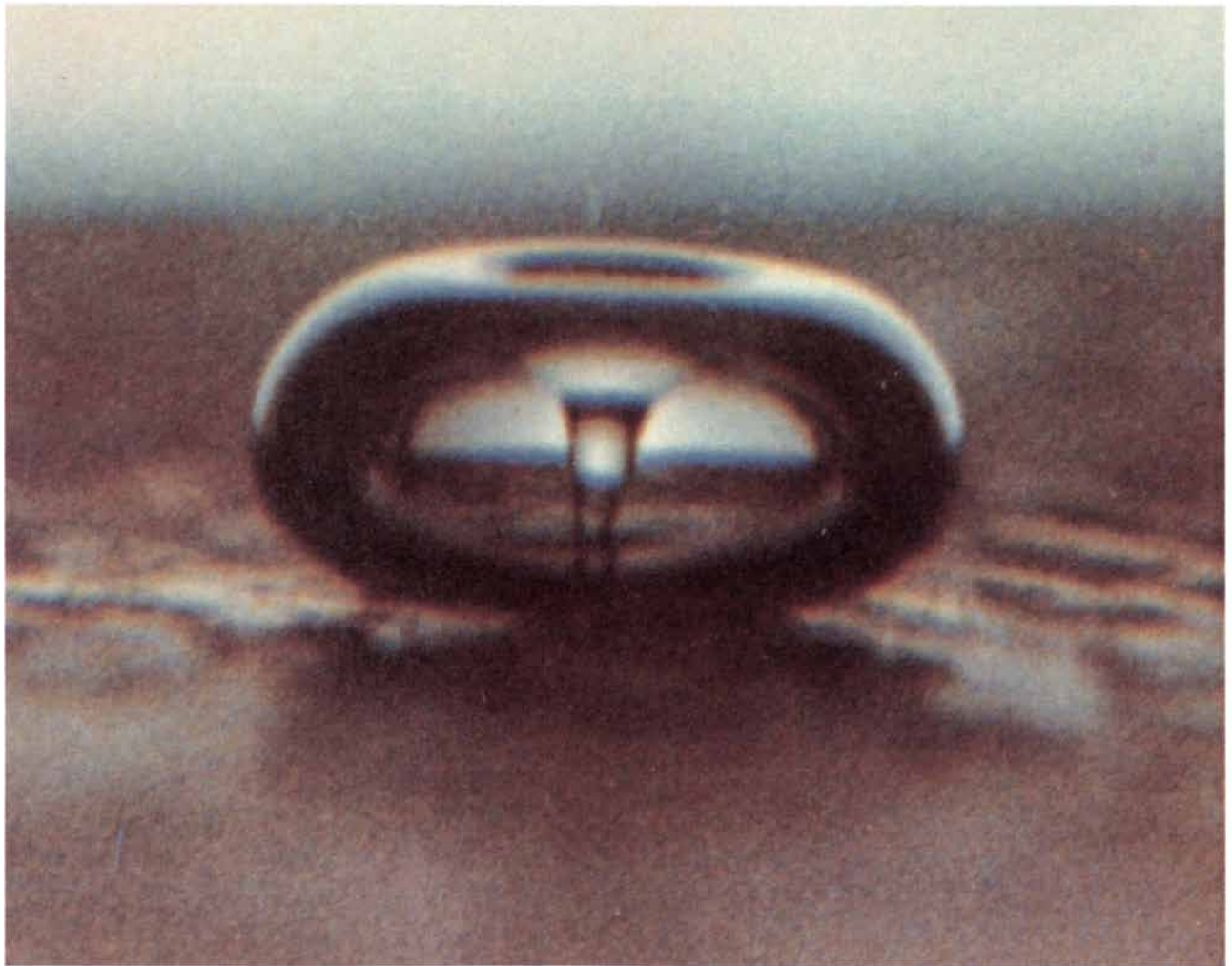
In other cases the average size of the bubble will increase.

Cavity growth depends on the intensity of sound. High-intensity ultrasound can expand the cavity so rapidly during the negative-pressure cycle that the cavity never has a chance to shrink during the positive-pressure cycle. In this process, therefore, cavities can grow rapidly in the course of a single cycle of sound.

For low-intensity ultrasound the size of the cavity oscillates in phase with the expansion and compression cycles. The surface area of a cavity produced by low-intensity ultrasound

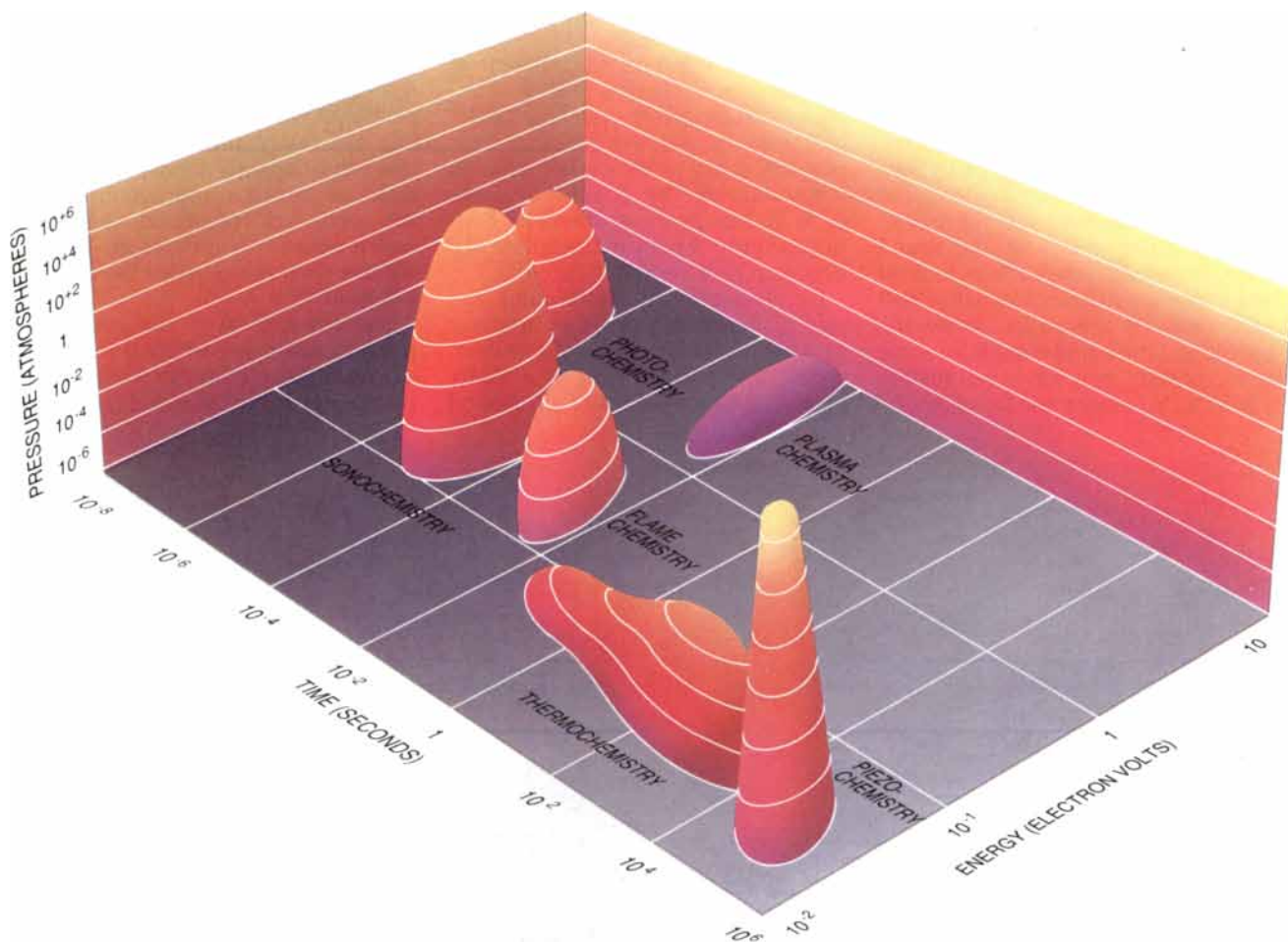
is slightly greater during expansion cycles than during compression cycles. Since the amount of gas that diffuses in or out of the cavity depends on the surface area, diffusion into the cavity during expansion cycles will be slightly greater than diffusion out during compression cycles. For each cycle of sound, then, the cavity expands a little more than it shrinks. Over many cycles the cavities will grow slowly.

The growing cavity can eventually reach a critical size where it will most efficiently absorb energy from the ultrasound. The critical size depends on



IMPLoding CAVITY in a liquid irradiated with ultrasound is captured in a high-speed flash photomicrograph (*above*). The implosion heats the gases inside the cavity to 5,500 degrees Celsius. Since this cavity formed near a solid surface, the implosion is asymmetric, expelling a jet of liquid at roughly 400 kilometers per hour. Both the heat and the jet contribute to a unique chemical environment in the liquid. The diameter of the cavity is about 150 microns. The drawing (*left*) shows the stages of cavity implosion and the formation of the jet. The cavity is spherical at first and then shrinks rapidly. The jet develops opposite the solid surface and moves toward it.





SONOCHEMISTRY makes available a range of energies as well as combinations of pressure and duration not available from any other source. The relations among energy, pressure and time are shown for sonochemistry and other chemistry fields.

the frequency of the ultrasound wave. At 20 kilohertz, for example, the critical size is a cavity roughly 170 microns in diameter. At this point the cavity can grow rapidly in the course of a single cycle of sound.

Once a cavity has experienced a very rapid growth caused by either low- or high-intensity ultrasound, it can no longer absorb energy as efficiently from the sound waves. Without this energy input the cavity can no longer sustain itself. The liquid rushes in and the cavity implodes.

The implosion of cavities establishes an unusual environment for chemical reactions. The gases and vapors inside the cavity are compressed, generating intense heat that raises the temperature of the liquid immediately surrounding the cavity and creates a local hot spot. Even though the temperature of this region is extraordinarily high, the region it-

self is so small that the heat dissipates quickly. My co-workers and I at the University of Illinois at Urbana-Champaign estimate that the heating and cooling rates during cavitation are more than a billion degrees C per second! This is similar to the cooling that occurs if molten metal is splattered onto a surface cooled near absolute zero. At any given time, therefore, the bulk of the liquid remains at the ambient temperature.

The exact temperatures and pressures generated during cavity implosion are difficult both to calculate theoretically and to determine experimentally. Yet these quantities are fundamental to describing the potential of sonochemistry. Theoretical models have been proposed that approximate the dynamics of cavity implosion at various levels of accuracy. All have difficulty accurately describing cavity dynamics during the last stages of implosion. The most sophis-

ticated models give temperatures of thousands of degrees Celsius, pressures of from hundreds to thousands of atmospheres and heating times of less than a microsecond.

The temperature of the imploding cavity cannot be measured with a physical thermometer because the heat is dissipated too quickly to be registered. Recently my collaborators and I found an alternative that enables one to check theoretical results experimentally. One way to gauge temperature is to observe the rate at which familiar chemical reactions take place. More precisely, the temperature is related to the negative inverse logarithm of the rate of the reaction. If the rates of several different reactions are measured in an ultrasound environment, the temperature from cavity implosion can be calculated.

In the process of determining the relative rates of a series of sonochemical reactions, David A. Hammerton in

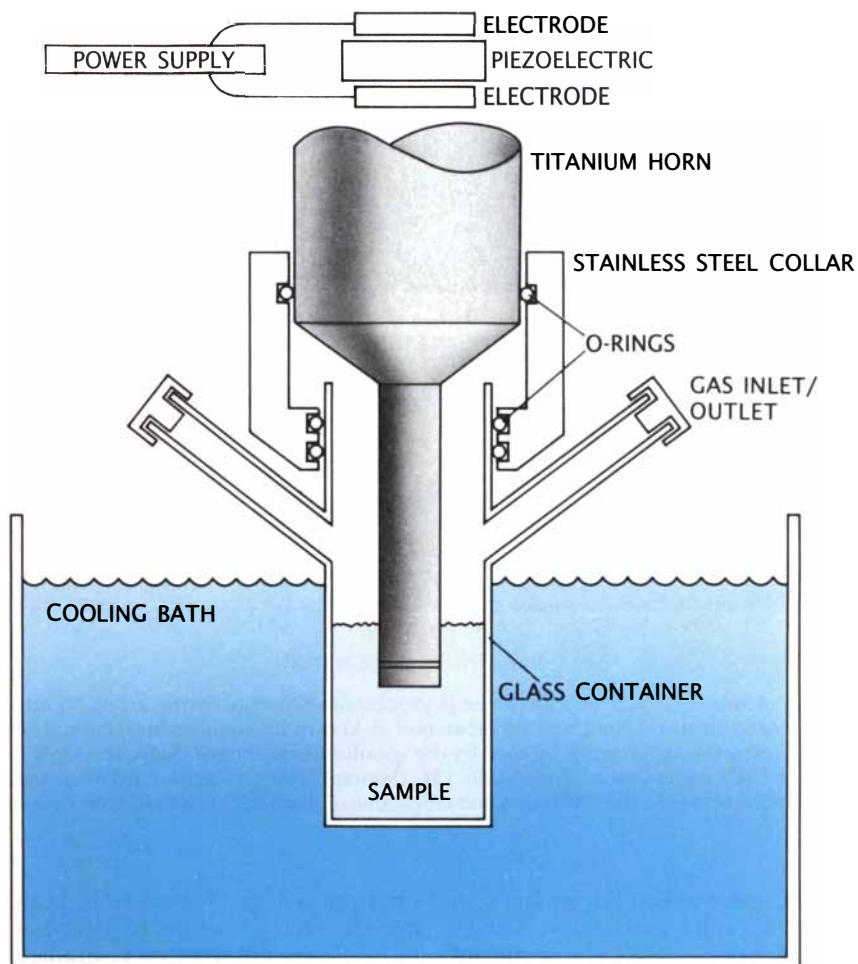
our laboratory discovered two distinct temperature regions associated with cavity implosion. The original gaseous contents of the cavity reached temperatures of about 5,500 degrees C, whereas the liquid immediately surrounding the cavity reached 2,100 degrees. The temperature of the flame from an acetylene torch, in comparison, is about 2,400 degrees.

Although the pressures attained during cavity implosion are harder to determine experimentally than temperature, the two quantities are correlated. One can therefore estimate the peak pressure to be 500 atmospheres, which is half the pressure at the deepest region of the ocean, the Mariana Trench.

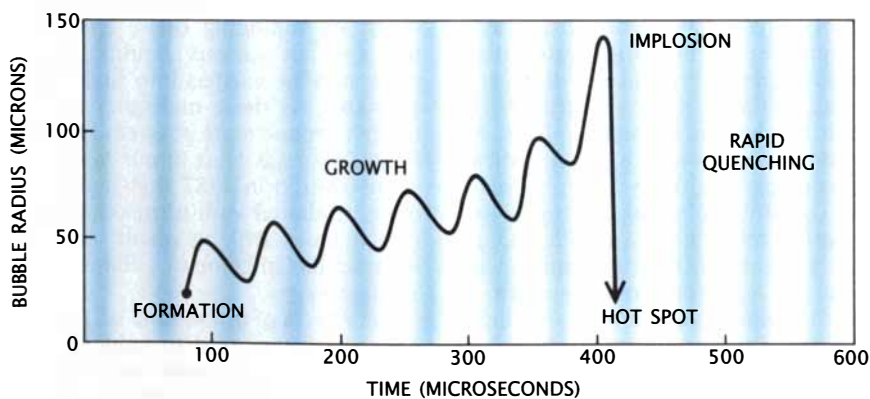
Even though the local temperature and pressure conditions created by cavity implosion are extreme, chemists have good control over sonochemical reactions. The intensity of cavity implosion, and hence the nature of the reaction, can easily be altered by such factors as acoustic frequency, acoustic intensity, ambient temperature, static pressure, choice of liquid and choice of ambient gas. The way these factors alter sonochemistry often defies basic intuitions about chemistry. Let me cite three examples.

First, unlike virtually all chemical reactions, most sonochemical reactions decrease in rate with increasing ambient temperature—that is, the temperature outside the cavity. The higher the ambient temperature is, the more vapor there will be inside the cavity. The extra vapor cushions the implosion of the cavity and lowers the temperature of implosion. Therefore sonochemical reactions proceed more slowly as ambient temperature increases. Second, unlike chemical events driven by light, sonochemical reactions do not depend greatly on frequency. The major effect of frequency is to change the critical size of a cavity before implosion, which does not change the cavitation process significantly. Third, unlike many chemical reactions in solution, the ambient gas that is dissolved in the liquid is quite important. If xenon fills a cavity, the peak temperature reached during cavity implosion will be high because xenon conducts heat poorly and retains the heat of the collapsing cavity. Helium, on the other hand, conducts heat so well that it can virtually shut down sonochemical reactions.

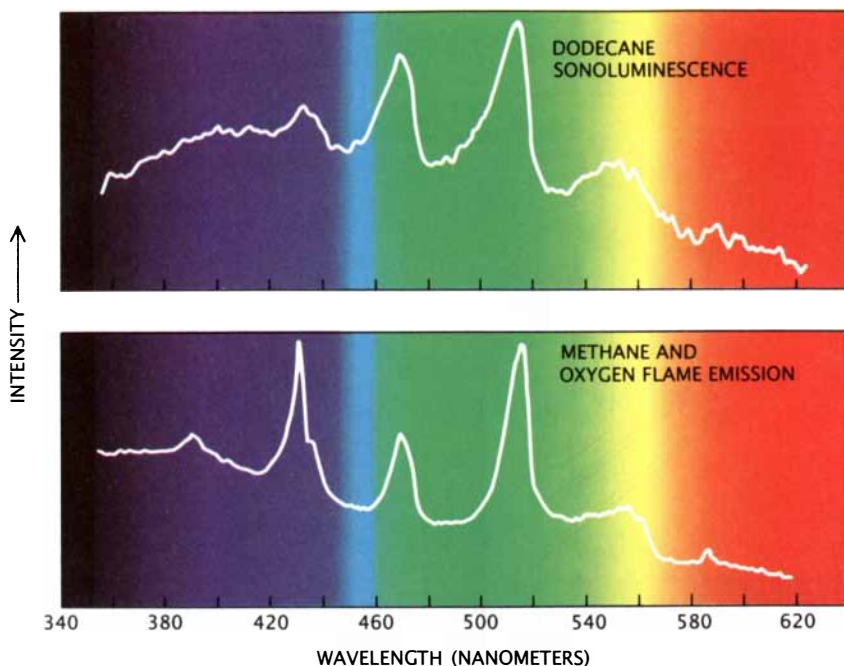
The dynamics of cavity growth and implosion are strongly dependent on local conditions, including the form of the materials: whether they are



ULTRASONIC IMMERSION HORN is the intensest generator of ultrasound in general use. Ultrasound is produced in liquids by means of piezoelectric or magnetostrictive materials: materials that expand or contract when they are placed in electromagnetic fields. Exposing such materials to a field alternating at an ultrasonic frequency produces ultrasound. In the ultrasonic horn there is a piezoelectric ceramic attached to a tapered titanium rod, which serves to amplify the sound. The horn vibrates at a fixed acoustic frequency, typically 20 kilohertz, but the intensity is variable. Since power outputs are quite high, the reaction solution must be cooled.



BUBBLE GROWTH AND IMPLOSION in a liquid irradiated with ultrasound is the physical phenomenon responsible for most sonochemistry. Intense ultrasound waves generate large alternating stresses within a liquid by creating regions of positive pressure (*dark color*) and negative pressure (*light color*). A cavity can form and grow during the episodes of negative pressure. When the cavity attains a critical size, the cavity implodes, generating intense heat and tremendous pressure.



LIGHT resembling that from a gas flame is generated when cold hydrocarbon liquids are exposed to ultrasound; the phenomenon is known as sonoluminescence. The graphs show the spectrum produced by the sonoluminescence of dodecane, $C_{12}H_{24}$ (top), and the combustion of methane, CH_4 (bottom). The similarities between the spectrums are due to the formation and emissions of diatomic carbon in both cases.

liquids, extended solid surfaces in liquids or solid particles in liquids. In each case, because the dominant physical effects from cavity implosion differ, the chemistry changes as well.

The sonochemistry of liquids depends mainly on physical effects of the quick heating and cooling caused by cavity implosion. For instance, when Peter Riesz and his colleagues at the National Cancer Institute irradiated water with ultrasound, they proved that the heat from cavity implosion decomposes water (H_2O) into extremely reactive hydrogen atoms (H^\bullet) and hydroxyl radicals (OH^\bullet). During the quick cooling phase, hydrogen atoms and hydroxyl radicals recombine to form hydrogen peroxide (H_2O_2) and molecular hydrogen (H_2). If other compounds are added to water irradiated with ultrasound, a wide range of secondary reactions can occur. Organic compounds are highly degraded in this environment, and inorganic compounds can be oxidized or reduced.

Other organic liquids also yield interesting reactions when they are irradiated with ultrasound. For example, alkanes, major components of crude oil, can be "cracked" into smaller, desirable fragments, such as gasoline.

Crude oil is normally cracked by heating the entire mixture to temperatures above 500 degrees C. Irradiating alkanes with ultrasound, however, makes cracking possible at room temperature and produces acetylene, which cannot be produced through simple heating.

Perhaps the most unusual chemical phenomenon associated with ultrasound is its ability to produce microscopic flames in cold liquids by a process known as sonoluminescence. When an imploding cavity creates a hot spot in various liquids, molecules may be excited into high-energy states. As these molecules return to their ground state, they emit visible light. Edward B. Flint in our laboratory discovered in 1987 that hydrocarbons irradiated with ultrasound provide a most striking result: emitted light similar in color to a flame from a gas stove.

The effects of ultrasound on liquids have also been used to enhance the chemistry of compounds in solution. Compounds that contain metal-carbon bonds, called organometallics, are particularly illustrative. This diverse class of chemicals is important in the formation of plastics, in the production of microelectronics and in the synthesis of pharmaceuticals, herbi-

cides and pesticides. In 1981 Paul F. Schubert and I first investigated the effects of ultrasound on organometallics, in particular iron pentacarbonyl, or $Fe(CO)_5$. The results, when compared with the effects of light and heat on $Fe(CO)_5$, underscore the distinctive chemistry that ultrasound can induce [see illustration on opposite page]. When $Fe(CO)_5$ is exposed to heat, it decomposes into carbon monoxide (CO) and a fine iron powder, which ignites spontaneously in air. When $Fe(CO)_5$ is exposed to ultraviolet light, it first breaks down into $Fe(CO)_4$ and free CO fragments. $Fe(CO)_4$ can then recombine to form $Fe_2(CO)_9$. Cavity implosion creates different results. It delivers enough heat to dissociate several CO molecules but cools quickly enough to quench the reaction before decomposition is complete. Thus when $Fe(CO)_5$ is exposed to ultrasound, it yields the unusual cluster compound $Fe_3(CO)_{12}$.

The sonochemistry of two immiscible liquids (such as oil and water) stems from the ability of ultrasound to emulsify liquids so that microscopic droplets of one liquid are suspended in the other. Ultrasonic compression and expansion stress liquid surfaces, overcoming the cohesive forces that hold a large droplet together. The droplet bursts into smaller ones, and eventually the liquids are emulsified.

Emulsification can accelerate chemical reactions between immiscible liquids by greatly increasing their surface contact. A large contact area enhances crossover of molecules from one liquid to the other, an effect that can make some reactions proceed quickly. Emulsifying mercury with various liquids has particularly interesting chemistry as delineated by the investigations of Albert J. Fry of Wesleyan University. He developed the reactions of mercury with a variety of organobromide compounds as an intermediate in the formation of new carbon-carbon bonds. Such reactions are critical in the synthesis of complex organic compounds.

The sonochemistry of solid surfaces in liquids depends on a change in the dynamics of cavity implosion. When cavitation occurs in a liquid near an extended solid surface, the cavity implosion differs substantially from the symmetrical, spherical implosion observed in liquid-only systems. The presence of the surface distorts the pressure from the ultrasound field so that a cavity implosion near a surface is markedly asymmet-

ric. This generates a jet of liquid directed at the surface that moves at speeds of roughly 400 kilometers per hour. The jet, as well as the shock waves from cavity implosion, erode solid surfaces, remove nonreactive coatings and fragment brittle powders. Reactions are further facilitated by high temperatures and pressures associated with cavity implosion near surfaces. These processes all enhance the chemical reactivity of solid surfaces, which is important in the synthesis of drugs, specialty chemicals and polymers.

The sonochemistry of solid surfaces in liquids is best exemplified by reactions of active metals, such as lithium, magnesium, zinc and aluminum. Ultrasonic irradiation of reaction mixtures constituting these metals provides better control at lower temperatures and produces relatively higher yields. Pierre Renaud of the University of Paris first examined such reactions. More recently Jean-Louis Luche of the University of Grenoble and Philip

Boudjouk of North Dakota State University have popularized the use of an ultrasonic cleaning bath to accelerate the reactions of active metals.

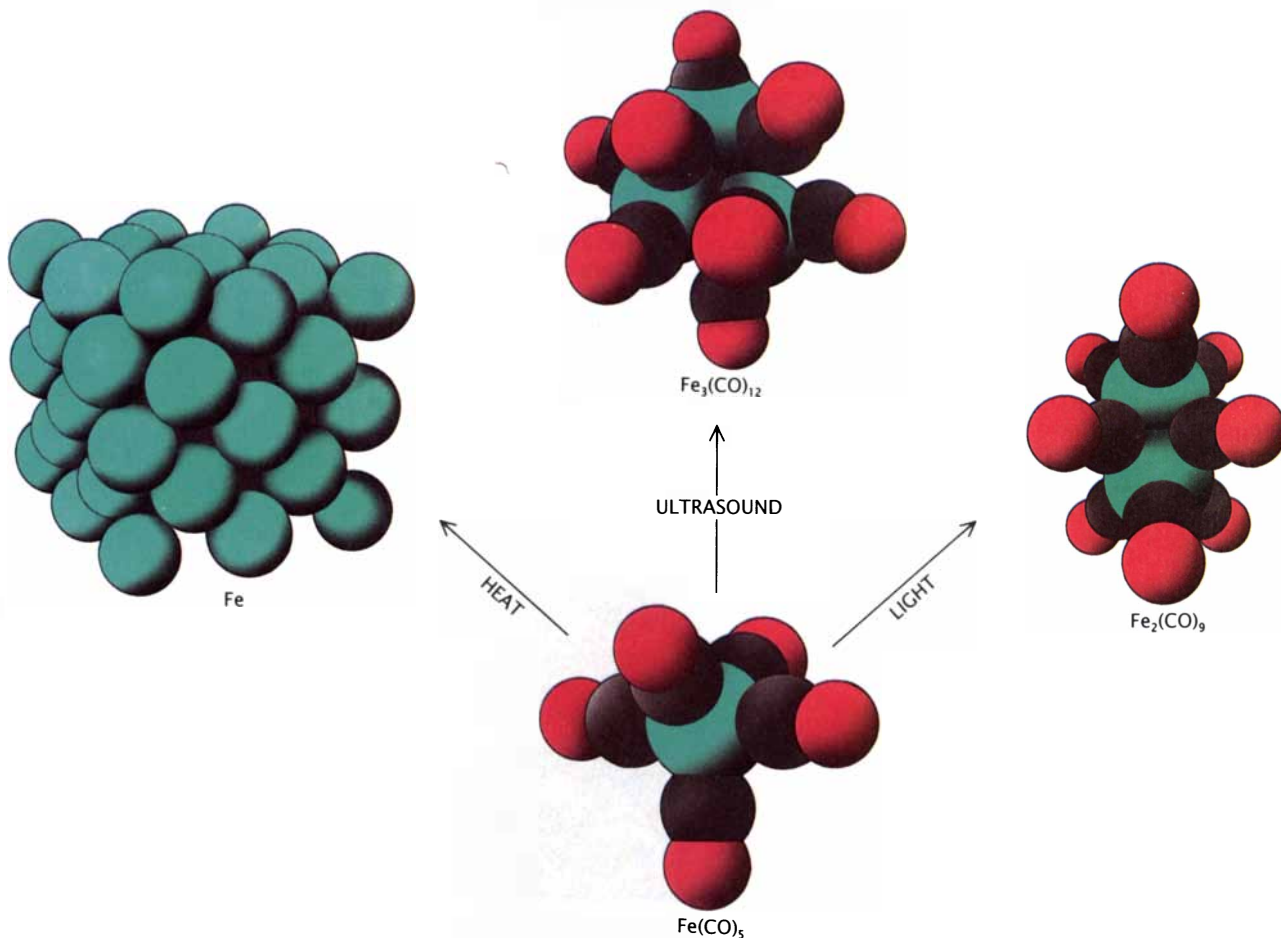
The chemistry of these metals is very difficult to control. Traces of water, oxygen or nitrogen can react at the surface to form protective coatings. Increasing the reactivity of the protected surface by direct heating, however, can result in undesirable explosions. Ultrasound can keep the surface clean and allows the reaction to proceed evenly at reduced ambient temperatures. Excellent yields and improved reliability can be achieved for many reactive metals in large-scale industrial applications.

The extreme conditions generated by cavitation near surfaces can also be utilized to induce reactivity in "unreactive" metals. Robert E. Johnson in our laboratory, for instance, examined reactions between carbon monoxide and molybdenum and tantalum, as well as other comparable metals. Conventional techniques require pres-

ures of from 100 to 300 atmospheres and temperatures of from 200 to 300 degrees C. to form metal carbonyls. Using ultrasound, however, formation of metal carbonyls can proceed at room temperature and pressure.

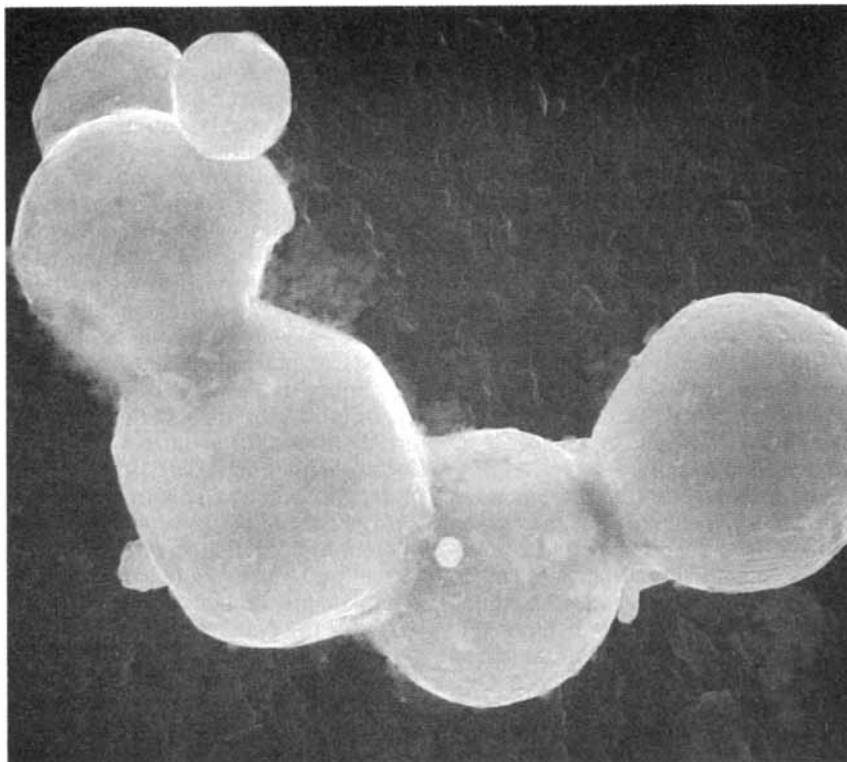
The implosion of a cavity, in addition to all the effects described so far, sends shock waves through the liquid. The sonochemistry of solid particles in liquids depends heavily on these shock waves; they drive small particles of a powder into one another at speeds of more than 500 kilometers per hour. My co-workers and I have recently shown that such collisions are so intense in metal powders that localized melting takes place at the point of impact. This melting improves the metal's reactivity, because it removes metallic-oxide coatings. (Such protective oxide coatings are found on most metals and are responsible for the patina on copper gutters and bronze sculpture.)

Since ultrasound improves the reactivity of metal powders, it also makes



CHEMISTRY OF ULTRASOUND can differ greatly from the chemistries of light and heat. The reactions of iron pentacarbonyl $\text{Fe}(\text{CO})_5$, an iron atom (green) bonded to five carbon monoxide units (gray and red), exemplify the differences. Heat decom-

poses iron pentacarbonyl into pure iron and carbon monoxide. Light yields two iron atoms bonded to nine carbon monoxide units. Ultrasound produces the cluster compound consisting of three iron atoms bonded to 12 carbon monoxide units.

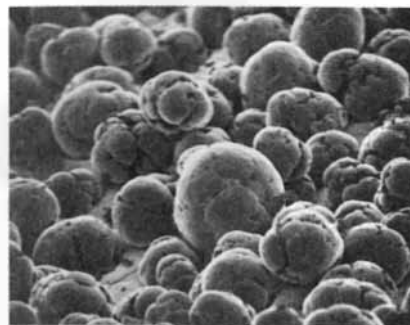
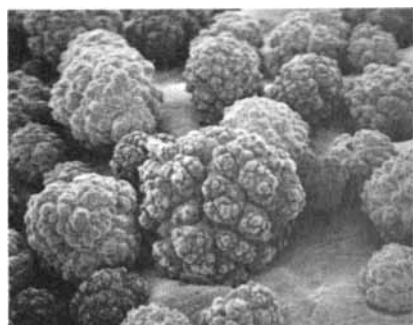


INTERPARTICLE COLLISIONS driven by shock waves from cavity implosion cause particles to agglomerate. The collisions between particles of zinc (here magnified 13,000 diameters) were so violent that the zinc particles melted on impact.

them better catalysts. Many reactions require a catalyst in order to proceed at useful or even appreciable rates. Catalysts are not consumed by the reaction but instead speed the reaction of other substances.

The effects of ultrasound on particle morphology, surface composition and catalyst reactivity have been investigated by Dominick J. Casadonte and Stephen J. Doktycz in our laboratory. They have discovered that catalysts

such as nickel, copper and zinc powders irradiated with ultrasound show dramatic changes in surface morphology. Individual surfaces are smoothed and particles are consolidated into extended aggregates. An experiment to determine the surface composition of nickel revealed that its oxide coating was removed, greatly improving the reactivity of the nickel powder. Ultrasonic irradiation increased the effectiveness of nickel powder as a catalyst



METAL SURFACES can be physically altered by ultrasound. Before this sample of nickel powder was irradiated with ultrasound (left) it had an unreactive crystalline coating on its surface. After irradiation (right) the coating was gone, exposing the nickel and boosting its reactivity. Without the coating the nickel powder becomes an excellent catalyst for chemical reactions. The magnification is about 100 diameters.

more than 100,000 times. The nickel powder is as reactive as some special catalysts currently in use, yet it is nonflammable and less expensive.

Ultrasound is a useful tool in nearly every case where a liquid and a solid must react. Furthermore, since ultrasound can radiate through large volumes of liquid, it is well suited for industrial applications. For these reasons future applications of ultrasound in chemical reactions will be diverse. In the synthesis of pharmaceuticals, ultrasound will improve chemical yields over conventional methods.

The greatest advances in sonochemistry, however, may be in the production of new materials that have unusual properties. The extraordinary temperatures and pressures reached during cavitation, for example, may lead to the synthesis of refractory materials (such as carborundum, tungsten carbide and even diamond). Refractory solids have high temperature stability and enormous structural strength. They are important as industrial abrasives and hardened tool bits.

The extremely rapid cooling that follows cavity implosion may be employed to create metallic glasses. Such amorphous metals have outstanding corrosion resistance and unusually high strength.

Although chemical applications of ultrasound are still in the early stages of development, the next few years promise rapid progress in sonochemistry. The use of ultrasound in laboratory reactions is becoming commonplace, and the extension of the technology to industrial-scale reactions is likely to follow. Underlying these developing technologies are the recent advances in our understanding of the nature of cavitation and the chemical effects of ultrasound.

FURTHER READING

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