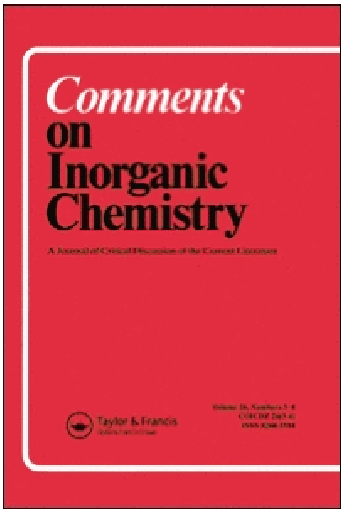

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Inorganic and Organometallic Synthesis with Ultrasonic Waves

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Inorganic and Organometallic Synthesis with Ultrasonic Waves

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The effects of ultrasonic waves on chemical reactions, increasingly referred to as sonochemistry, are reviewed here with a prejudice towards those transformations that are of interest to inorganic and organometallic chemists. Some of the fundamental concepts of ultrasonic waves in liquid media are also treated because they are essential to an understanding of the observed effects. A brief history of early developments in the field is also given.

Key Words: *ultrasound, heterogeneous sonochemistry, hydrosilyation, catalysis, polysilanes, activated metals, reductive coupling*

INTRODUCTION

Some Early Studies of Chemical Effects of Ultrasonic Waves

The pioneering work on the chemical applications of ultrasound was conducted in the 1920's by Richards and Loomis in their classic survey of the effects of high frequency sound waves on a variety of solutions, solids and pure liquids.[1] Ultrasonic waves are usually defined as those sound waves with a frequency of 20 kHz or higher.

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The human ear is most sensitive to frequencies in the 1–5 kHz range with upper and lower limits of 0.3 and 20 kHz, respectively.

Using quartz crystals of 6 to 12 millimeters in thickness and 50 to 80 millimeters in diameter held between two electrodes under oil, Loomis and his co-workers produced high intensity ultrasonic waves at frequencies of approximately 280 kHz. The high intensities are the result of the ability to generate voltages in the range of 50,000 with this configuration since the amplitude of vibration of quartz crystal increases directly with the voltage applied to it. With power levels of approximately 2 kilowatts readily available, investigation of the effects of ultrasonic waves on chemical systems became feasible. Table I summarizes their observations.

Mechanistic Considerations

Cavitation. The chemical effects observed by Loomis (see Table I) and those reviewed later in this article are largely the result of acoustic cavitation (see Fig. 1), i.e., the formation and collapse of bubbles in the liquid and consequent release of energy. When ultrasonic waves are passed through a medium, the particles experience oscillations which lead to regions of compression and rarefaction. The negative pressure in the rarefaction region disrupts the structure of the liquid leading to the formation of bubbles

TABLE I

Summary of Loomis' preliminary survey of the chemical effects of ultrasonic waves[1]

System	Effects of Ultrasonic Waves
Nitrogen triiodide	Rate of explosion accelerated
Superheated liquids	Rate of evaporation accelerated
Conversion of yellow HgI to red HgI	Rate of conversion accelerated
"Atomization" of liquids and solids	Rate of "atomization" of mercury and glass in water accelerated
Gases dissolved in water	Rate of expulsion of gases increased
Hydrolysis of methyl sulfate	Rate of hydrolysis increased
The "iodine clock" reaction	Rate of reduction of iodate by sulfite was increased
Boiling points of liquids	"Apparent" depression of boiling point

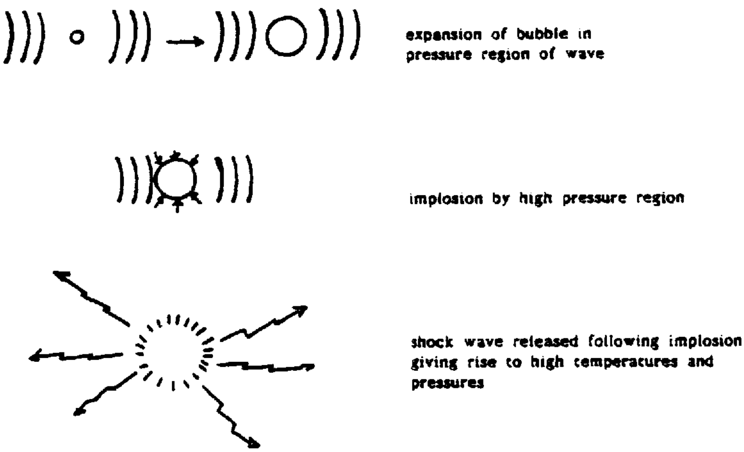


FIGURE 1 Acoustic cavitation.

which may be filled with a gas, the vapor of the liquid, or be almost empty depending on the vapor pressure and the forces holding the liquid together. Strictly defined, cavitation refers only to the completely evacuated bubble or cavity, a true void, but since dissolved gases are present unless special steps are taken to remove them, and the vapor of the liquid can also penetrate the cavity, the term cavitation most often encompasses the three kinds of bubbles.

The collapse of these bubbles, caused by the compression portion of the ultrasonic wave, produces powerful shock waves. The energy output in the region of the collapsing bubble is considerable, with temperatures of 5200 K in the gas phase reaction zone and 1900 K in the liquid layer (~200 nm thick) surrounding the bubble.[2] These temperature pulses, which are accompanied by shock waves with pressures in the 1–10 kilobar range, have lifetimes of approximately 10^{-8} sec.

Cavitation erosion. Cavitation erosion is predominantly mechanical in nature and has two possible sources: the shock wave of isolated imploding cavities attached to the surface and the jet impact generated by clusters of cavities collapsing near the surface. The relative importance of these effects has not been determined unequivocally. The most popular theory is that erosion of metals results from asymmetric collapse of single bubbles attached to, or very near, the surface which produces shock waves and liquid jets of sufficient force to deform the surface of the metal.[3-5]

As early as 1944, Kornfeld and Suvorov proposed that cavitation damage might be due to liquid jets produced by a collapsing bubble attached to a surface.[6] The first experimental evidence for this phenomenon came from Naudé and Ellis in 1961.[7] In 1966, Benjamin and Ellis concluded that the nonspherical collapse of single cavities led to impact jets of sufficient energy to cause damage on a solid surface and that spherical collapse of cavities occurs only at distances so far from the solid that damage is minimal.[8]

Calculations by Plesset and Chapman support these conclusions.[9] They estimated that little or no effect will be registered on the solid surface if the distance between the solid and the collapsing bubble is greater than $b/R_0 = 1.5$, where b is the distance from the center of the bubble of radius R_0 to the surface wall. At $b/R_0 = 1$, i.e., when the cavity touches the surface, the energy from collapse of the cavity is transferred into kinetic energy of the liquid jet and this energy is directed *toward* the wall. Figure 2 compares the two cases. Liquid jet velocities of 130 m/s leading to impact pressures of 2 kbar were calculated with this model. The pressure is applied to an area smaller than the cross section of the jet for a time period that does not exceed the ratio of the radius of the jet to the sound velocity. For a 1 mm cavity this is about 10^{-8} sec.

Brunton obtained photographs of the collapse of single attached bubbles produced by a vibration device demonstrating the effects of asymmetrical collapse.[10] Photographic data (Fig. 3) led to the calculation of jet velocities of approximately 500 m/s and shock pressures of about 5 kbar for involuting bubbles, or nearly twice that if the bubble is attached and the jet impacts the surface directly. Following collapse the bubble begins to expand again causing a flow of liquid towards the jet. The hydrodynamic pressure resulting from this flow, while smaller than the shock wave, has a longer lifetime and can be significant, especially for detached bubbles. For collapsing bubbles near a crack in the surface the expansion phase can lead to significant damage because the bubble can be wedged into the crack enlarging it and eventually causing fragmentation. Brunton sees three causes of erosion: impact of the intruding wall of the attached bubble; shock wave damage from the implosion; and flow against the surface during expansion of

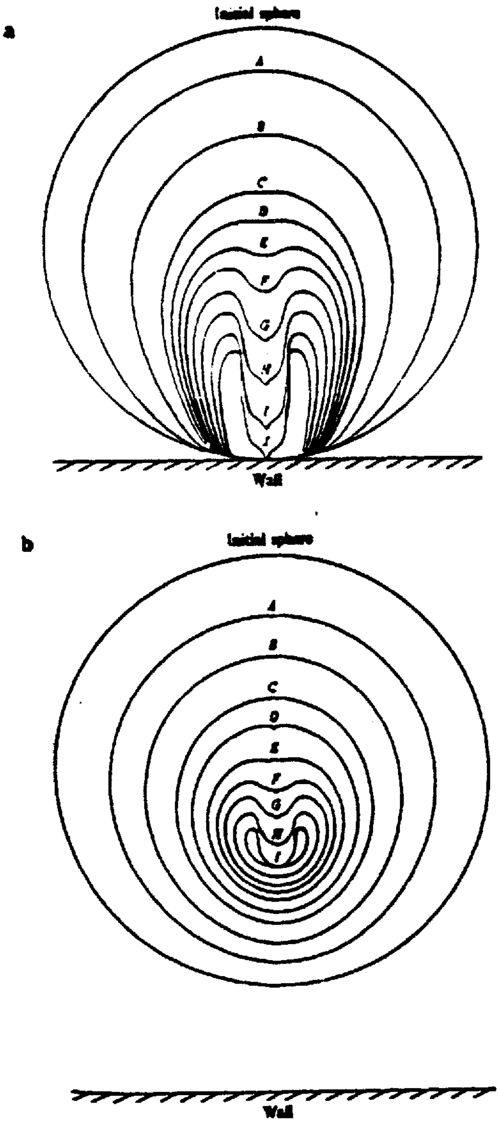


FIGURE 2 Calculated shapes of bubble implosion (Ref. 9). (a) attached bubble, (b) detached bubble.

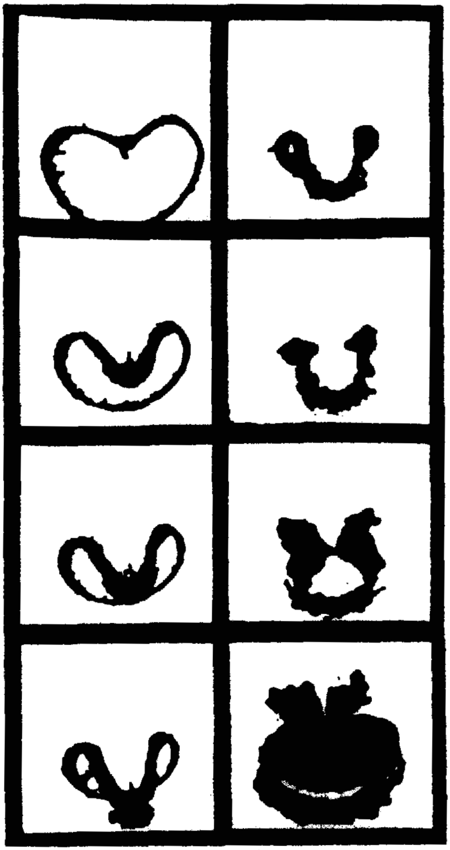


FIGURE 3 The asymmetric collapse of an attached bubble (Ref. 10).

the bubble. Of these, the first is generally viewed as the most important.

Single bubbles detached from a surface can also cause erosion. Using laser generated bubbles and high speed photography, Lauterborn and Bolle[11] recorded the growth and collapse of bubbles near a solid boundary. As shown in Fig. 4, the shape of a bubble is distorted by a nearby surface as it collapses toward implosion. Instead of a spherical collapse a vanishing bubble near a solid develops a peak or tip directed toward the surface that eventually "touches down," generating a liquid jet at the surface.

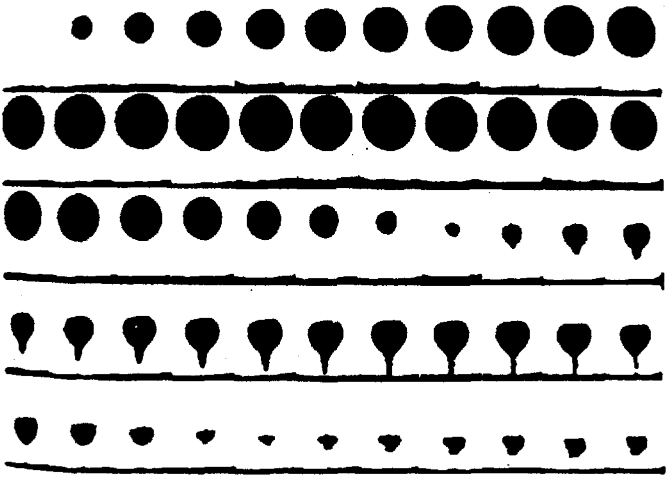


FIGURE 4 Laser generated bubbles near a solid surface (Ref. 11).

The asymmetry in the collapsing bubble is the result of the distortion of the ultrasonic field surrounding the bubble near the solid. The diminished pressure between the surface and the oscillating bubble prevents "upward" movement of the lower part of the bubble leading to the bulge at the bottom. Once started, the process is irreversible and the tip grows toward the surface. Lauterborn and Bolle[11] achieved nearly quantitative agreement with Plesset and Chapman[9] in their comparison of the experimentally observed stages of bubble collapse and the calculated shapes of the bubble during implosion. Velocities of liquid jets at the tip exceeded 100 m/sec. These velocities are also in accord with theory[9] and are attributed to the high radius of curvature at the tip. In addition to the jet impact produced by the collapsing cavity, a shock wave of 1–10 kbar is also generated.

As the distance between the wall and the collapsing bubbles increases the bubbles become more spherical and their collapse becomes more symmetrical.[12] This leads to an increasing fraction of energy emitted in the form of a spherical wave, which is partly responsible for reduced impact at larger distances from the wall. This was verified by Lauterborn who showed, using holographic techniques, that collapsing spherical bubbles generate spherical shock waves.[13]

Gaining acceptance is the theory that a cluster of bubbles collapsing in concert at a distance from the surface may be an important mechanism for energy transfer to a solid.[4,5] Vyas and Preece have measured pressures up to 9 kbar from the simultaneous collapse of a cavity cloud generated by an ultrasonic horn.[14] A series of concerted collapses of large numbers of bubbles is more likely responsible for the formation of long slip lines (>1 cm),[15] the growth of large craters[16] and the depth of work-hardening[17] in some metals and alloys than are isolated implosions of single bubbles.

Acoustic streaming. Cavitation improves mixing but, on a macroscopic scale, it is probably less effective than a high speed stirrer. However, the absorption of sound energy by a solid induces a time-independent flow of fluid at the surface called acoustic streaming which enhances mass transport to the solid surface. This leads to higher reaction rates by increasing the rate at which the depleted concentration of reagents at the solid surface is replenished.

Early Applications in Inorganic Chemistry

In the early thirties, Freundlich and Sollner embarked on a series of investigations of the effects of ultrasonic waves on gels, discovering that thixotropic gels of iron and aluminum oxide could be liquified and that the process is initiated at the liquid–air interface.[18] In a related study, Sata and Watanabe were able to produce permanently dispersed iron hydroxide from the reaction of iron chloride and ammonia in water in the absence of a peptization agent while irradiating the reaction mixture with a frequency of 450 kHz.[19]

During this period, Moriguchi conducted a number of studies in which he observed that the reactions of strong acids were enhanced by ultrasonic waves. For example, the consumption of zinc by hydrochloric acid was accelerated[20]:

$$\mathrm{Zn} + 2\,\mathrm{HCl} \xrightarrow{)))} \mathrm{ZnCl_2} + \mathrm{H_2}$$

as was the reaction of calcium carbonate and sulfuric acid:

$$\mathrm{CaCO_3} + \mathrm{H_2SO_4} \xrightarrow{)))} \mathrm{CaSO_4} + \mathrm{H_2O} + \mathrm{CO_2}$$

and the reduction of copper sulfate by zinc to give colloidal copper[21]:

$$Zn + CuSO_4 \xrightarrow{)))} ZnSO_4 + Cu$$

He also observed that finely divided metal powders produced colloids when sonicated in water.[21]

Moriguchi was among the first to evaluate the effects of ultrasonic waves on electrochemical processes finding that irradiation eliminated overvoltage in the electrolytic reduction of copper sulfate, presumably by removal of the diffusion barrier between the electrode and the electrolyte.[22] Claus, using a cell in which the cathode and the electrolyte were vibrated with ultrasonic waves during the reduction of metal salts, produced fine dispersions of iron, silver and platinum.[23] However, conditions could be altered to produce high quality films of electrodeposited metal. Mueller, for example, used ultrasonic waves during the reduction of nickel, copper, chromium and brass and obtained bright films with finer grain texture and higher tensile strength than when they were deposited in the absence of ultrasonic irradiation.[24]

The effects of ultrasound on catalysts attracted widespread attention. As early as 1940, an attempt to improve the Haber process with ultrasonic equipment was tried, unsuccessfully. Pshenitsyn and co-workers reported that high frequency ultrasound (555 kHz) at 300 atmospheres failed to accelerate a mixed catalyst system[25]:

$$H_2 + N_2 + Fe_3O_4 + Al_2O_3 + K_2O \xrightarrow{)))} 2NH_3$$

However, a decade later, Richardson obtained a patent for increasing the yields of ammonia by irradiating 200 micron iron powder suspended in a gas stream of hydrogen and nitrogen at 100–200°C and 1–2 atmospheres pressure.[26] Yields of 29–32% per pass were reported on runs using 100 pounds of catalyst per 100 cubic feet of gas. Fastening iron wires to an ultrasonic driver and vibrating them in the longitudinal direction during exposure to the reactants also improves the process.[27] This approach is also useful for other reactions.

Coating wires with iron, platinum or nickel and coupling the wires to a transducer will accelerate not only the synthesis of ammonia but also the hydrogenation of unsaturated fats as well as the oxidations of sulfides to sulfur trioxide, carbon monoxide to carbon dioxide, methanol to formaldehyde, and ethanol to acetic acid.[28] Platinum, rhodium and palladium black will also catalyze ammonia formation and, in the presence of ultrasonic waves, the yields for each metal are 2–6.5 times greater with rhodium demonstrating the greatest overall activity.[29] Alloyed catalysts can also benefit from sonication: Graves and co-workers claimed in their 1966 patent that the efficiency of brass used in the reduction of acetone to isopropanol was increased from 63% to 82% using ultrasonic waves.[30]

The effect of ultrasonic waves on the reactions of hydrogen gas were studied by a number of workers. The ultrasonically accelerated reduction of carbon monoxide by hydrogen at low temperatures and low pressures was examined by Mayer and Marinesco in 1944.[31] Möckel found that pressure hydrogenation of olefins was improved by ultrasound and presented some experimental data supporting ultrasonic acceleration of hydrogenation in open vessels.[32] Using the traditional Raney Nickel catalyst, Saracco found that ultrasound greatly accelerates the hydrogenation of olive oil dissolved in cyclohexane or cyclohexanol.[33]

Destructive hydrogenation at low temperatures and pressures promoted by ultrasound was the subject of a French patent.[34] Using frequencies of 1–3 megacycles, Marinesco claimed that the autoclave that was normally required could be replaced in the hydrogenation of shale, lignite, coal, peat and petroleum residues. This technique was also applied successfully to the reduction of metal oxides and carboxylic acids by hydrogen to give the free metals and alcohols, respectively. Pchelkin and co-workers conducted a similar study on the reduction of iron ore pellets observing that hydrogen and carbon monoxide reductions were 1.7–1.8 times faster in the presence of ultrasonic waves and that the rate of reduction of Fe_2O_3 by carbon was accelerated by 20%.[35] Similarly, ultrasound enhanced the activity of a magnesium-promoted aluminum–nickel–molybdenum catalyst system used for the hydrogenolysis of organic sulfides by increasing the dispersity and effective surface area of the catalyst.[36] Increased rates and higher yields were observed for the hydrodesulfurization of thiophene and sulfur-containing hydrocarbon raw materials.

RECENT DEVELOPMENTS

Although there are precedents for the successful promotion of the reactions of metals with organic compounds in the work of Renaud on grignard reagents in 1950[37] and Slough and Ubbelohde on radical anions in 1951,[38] much of the recent interest in the chemical applications of ultrasonic waves was spurred by the efforts of three groups in late 1980 and early 1981: Luche (France), Suslick (USA) and Boudjouk (USA).

Luche described the beneficial effects (high yields, short reaction times, mild conditions) of ultrasound on the lithium promoted Barbier reaction[39]:

$$R'\text{-}X + Li + R_2C{=}O \xrightarrow{)))} R'R_2C\text{-}OH$$

Suslick demonstrated that sonication of solutions of alkenes and iron pentacarbonyl led to the catalytic isomerization of the alkenes[40]:

$$\text{1-alkene} + Fe(CO)_5 \xrightarrow{)))} \textit{cis-},\ \textit{trans-}\text{2-alkenes}$$

Boudjouk used ultrasonic waves to accelerate the lithium modified Wurtz reaction as well as the reductive coupling of chlorosilanes and chlorostannanes at approximately room temperature to prepare disilanes and distannanes[41]:

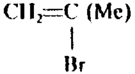
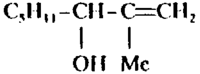
$$R_3MCl + Li \xrightarrow{)))} R_3M\text{-}MR_3$$

The results of these first modern applications of ultrasonic waves to chemical systems are summarized in Tables II, III and IV.

Reductive coupling of chlorosilanes. The synthesis of Si–Si linkages under mild conditions was readily extended to cyclic and linear polysilanes. The original report[41] on ultrasonically accelerated re-

TABLE II

Ultrasound promoted Barbier reaction

Organic Halide	Carbonyl Compound	Product	Reaction Time (min)	Yield (%)[a]
MeI			10	100 (92)
i-PrBr	p-MeOC$_6$H$_4$CHO	p-MeOC$_6$H$_4$CH(OH)i-Pr	15	100 (96)
n-BuBr	$(n\text{-Bu})_2C{=}O$	$(n\text{-Bu})_3C{-}OH$	15	100 (90)
c-C$_6$H$_{11}$Br	$Me_2C{=}O$	$Me_2(c\text{-}C_6H_{11})C{-}OH$	30	80 (68)
PhBr	$Me_2C{=}O$	$PhMe_2C{-}OH$	30	100 (95)
 $CH_2{=}\underset{Br}{C}(Me)$	$C_5H_{11}CHO$	 $C_5H_{11}{-}\underset{OH}{CH}{-}\underset{Me}{C}{=}CH_2$	40	96 (71)

[a] Yields estimated by VPC. Isolated yields are in parentheses.

TABLE III

Sonocatalytic isomerization of 1-pentene by iron carbonyls

Precatalyst (M)[a]	Rate of 2-Pentene[b] Formation	))), h[c]	Initial Turnover Rate
$Fe(CO)_5$ (0.1)	2.0×10^{-1}	1	4
$Fe(CO)_5$ (0.1)	$<1 \times 10^{-6}$	0	$<10^{-5}$
$Fe_2(CO)_9$ (0.01)	1.7×10^{-1}	1	51
$Fe_2(CO)_9$ (0.01)	$<2 \times 10^{-4}$	0	$<2 \times 10^{-2}$
$Fe_3(CO)_{12}$ (0.01)	1×10^{-2}	1	5
$Fe_3(CO)_{12}$ (0.01)	$<2 \times 10^{-4}$	0	$<2 \times 10^{-2}$

[a] Precatalyst dissolved in decane. 0°C. In the absence of 1-pentene ($Fe(CO)_5$ and $Fe_2(CO)_9$ produce $Fe_3(CO)_{12}$.

[b] *Trans/cis* ratio is always ~3.0.

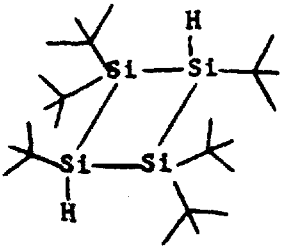
[c] Probe sonicator, 20 kHz, 100 W/Cm^2, 10mL reaction volume, Ar atmosphere.

ductive coupling included the facile preparations of dodecamethylcyclohexasilane and octaphenylcyclotetrasilane:

$$Me_2SiCl_2 + Li \xrightarrow{)))} (Me_2Si)_6$$

$$Ph_2SiCl_2 + Li \xrightarrow{)))} (Ph_2Si)_4$$

Subsequently, Masamune reported efficient ultrasonically promoted syntheses of novel strained cyclotrisilanes.[42] Condensations under mild conditions permit the isolation of gram quantities of a novel cyclotetrasilane from the reaction of di-t-butyldichlorosilane and lithium[43]:



The presence of two hydrogen functionalities on two silicon atoms will permit further chemistry on the ring. There is now only a very

TABLE IV

Ultrasound promoted reductive coupling of Group 14 halides

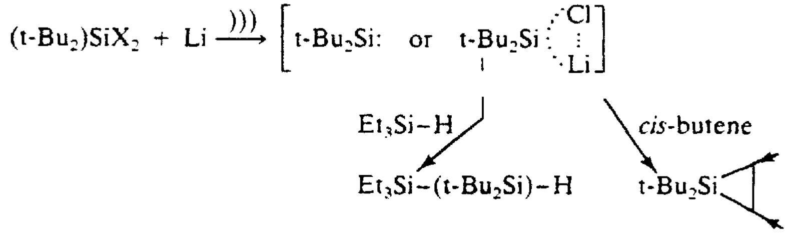
Halide	Product[a]	Yield (%)[b]
$C_6H_5-Cl(Br,I)$	$C_6H_5-C_6H_5$	85–90
C_6H_5-COCl	$C_6H_5C(O)-C(O)C_6H_5$	85–90
n-C_4H_9Cl	n-C_8H_{18}	85–90
Me_3SiCl	$Me_3Si-SiMe_3$	60–70
Et_3SiCl	$Et_3Si-SiEt_3$	90
Ph_3SiCl	$Ph_3Si-SiPh_3$	90
Ph_2HSiCl	$Ph_2HSi-SiPh_2H$	85
t-Bu_2HSiCl	t-$Bu_2HSi-Si(t$-$Bu)_2H$	80
Me_3SnCl	$Me_3Sn-SnMe_3$	60
n-Bu_3SnCl	n-$Bu_3Sn-Sn(n$-$Bu)_3$	94

[a] When Li dispersion or sand is used, reactions are complete in 30–60 minutes at room temperature. With Li wire yields are significantly lower (36–73%) and the reaction times longer (10–17 h). An ultrasonic bath (55 kHz, 150 Watts) was used.

[b] Glc yields. Isolated yields on prep scale runs (10–20 g) are 10–15% lower. In the absence of ultrasonic waves, stirred reactions often stopped at less than 50% conversion due to passivation of the lithium by salts. Heating the reactions to reflux give yields closer to ultrasonically promoted reactions but the product is usually contaminated.

limited substitution chemistry of cyclotetrasilanes and access to gram quantities of this compound should open up that arena.

Detailed studies of the reaction of di-t-butyldihalosilanes with lithium in the presence of suitable trapping agents reveal that the key reactive intermediate is di-t-butylsilylene or close analogue[43,44]:

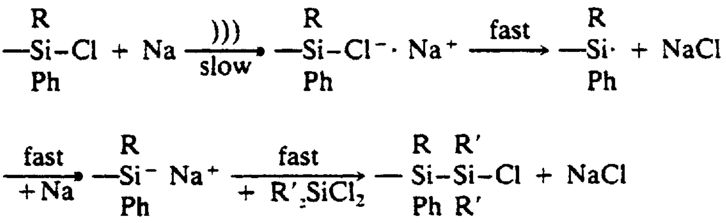


The clean, high yield reaction with *cis*-butene to form the *cis*-silacyclopropane is particularly informative because it provides strong evidence that the silylene (or silylenoid) has a singlet ground state and that the large t-butyl groups are not bulky enough to distort the silylene into a geometry, i.e., linear or nearly linear, that would stabilize the triplet state.

In the absence of ultrasonic waves, longer reaction times and/or higher temperatures are required. Higher temperatures inevitably lead to lower yields and contamination of the product(s) with siloxanes (compounds with Si–O–Si linkages) and silicon hydrides, which complicate purification and further reduce yields.

The technique has found successful application in the synthesis of novel polymers. Recently Weidman has reported the efficient synthesis of poly(n-hexylsilyne), the first alkyl silicon network polymer, using an ultrasonic probe.[45] Whereas conventional heterogeneous reductive condensation approaches require >100°C and high speed stirring and are usually hampered by incomplete reduction and rearrangements to complex product mixtures, this novel polymer ($M_w = 2.4 \times 10^4$, polydispersity = 2.1) was prepared in good yield (33%) under essentially ambient conditions.

Matyjaszewski has described the synthesis of several monomodal high molecular weight polysilanes by ultrasonically enhanced condensation reactions of phenyl substituted dichlorosilanes at ambient temperatures.[46] These results contrast with the usual methods of synthesis which lead to polymodal molecular weight distributions. Presumably ultrasound accelerates the slow first step in the pathway to Si–Si bond formation, i.e., electron transfer from sodium to chlorosilane:

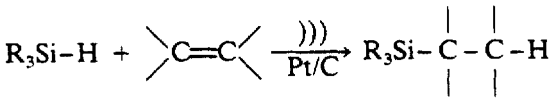


$$-\overset{R}{\underset{Ph}{Si}}-Cl + Na \xrightarrow[slow]{)))} -\overset{R}{\underset{Ph}{Si}}-Cl^{-}\cdot\,Na^{+} \xrightarrow{fast} -\overset{R}{\underset{Ph}{Si}}\cdot + NaCl$$

$$\xrightarrow[+Na]{fast} -\overset{R}{\underset{Ph}{Si}}{}^{-}\,Na^{+} \xrightarrow[+\,R'_2SiCl_2]{fast} -\overset{R}{\underset{Ph}{Si}}-\overset{R'}{\underset{R'}{Si}}-Cl + NaCl$$

Acceleration of the reduction step is attributable to either increased surface area from the dispersive action of ultrasonic waves or to a lower barrier to electron transfer as a result of ultrasonically cleaned sodium surfaces.

Hydrosilation. The addition of Si–H linkages across carbon–carbon double and triple bonds (hydrosilation) is an important route to preparing compounds with silicon–carbon bonds. The reaction is useful at the



$$R_3Si-H + \rangle C=C\langle \xrightarrow[Pt/C]{)))} R_3Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

bench and at the plant, covering the range from milligrams to tons. Wagner and Strother developed the first heterogeneous catalyst system (platinum) for hydrosilation in 1953.[47] The conditions were harsh (>100°C, >100 psi, >24 h) and the yields were not only low but the product mixtures were complex. Speier greatly improved the potential for the reaction by using the homogeneous catalyst, chloroplatinic acid, which gives high yields under very mild conditions.[48] Unfortunately, the platinum is not recoverable. Investigation of this reaction using platinum-on-carbon with ultrasound led to significant rate and yield enhancements.[49] Moreover, the catalyst is recyclable. The results are summarized in Table V.

Perhaps more significant is that we have been able to replace platinum with the much less expensive nickel.[50] Freshly prepared nickel powder will catalyze hydrosilation of 1-hexene in very high yields under mild conditions. Good yields are obtained with refluxing but induction times

$$NiI_2 + Li \xrightarrow{)))} Ni^* + LiI$$

$$C_4H_9-CH=CH_2 + H-SiCl_3 \xrightarrow{)))} \underset{90-100\%}{C_4H_9-CH_2-CH_2-SiCl_3}$$

are reduced and yields enhanced when the reactions are run in an ultrasonic cleaning bath. Typically, induction times of 10–30 min are followed by fast hydrosilation (5–15 min). The reaction is inhibited by excess olefin and by triphenylphosphine but enhanced by excess trichlorosilane. The nickel is recyclable showing no significant loss in efficiency after as many as six runs. Nickel powder from commercial sources does not catalyze hydrosilation even after

TABLE V

Ultrasonically accelerated hydrosilation catalyzed by platinum[a]

Alkene	Silane	Time, h	Product	Isolated Yield, %
1-hexene	$HSiCl_3$	1	n-$C_6H_{13}SiCl_3$	90
	$HSiMeCl_2$	1	n-$C_6H_{13}SiMeCl_2$	95
	$HSiEt_3$	2	n-$C_6H_{13}SiEt_3$	74
4-methyl-1-pentene	$HSiCl_3$	1	$(CH_3)_2CHCH_2CH_2CH_2SiCl_3$	94
	$HSiMeCl_2$	1	$(CH_3)_2CHCH_2CH_2CH_2SiMeCl_2$	96
	$HSi(OEt)_3$	1	$(CH_3)_2CHCH_2CH_2CH_2Si(OEt)_3$	93
styrene	$HSiCl_3$	1.5	$PhCH_2CH_2SiCl_3$	94
	$HSiMeCl_2$	1.5	$PhCH_2CH_2SiMeCl_2$	94

[a]Typical alkene:silane:Pt mole ratios were $0.05:0.1:5 \times 10^{-6}$.

extensive sonication. It should be noted, however, that Suslick has demonstrated that ultrasound greatly enhances the catalysis of hydrogenation by commercial nickel.[51]

In other hydrosilation studies, it was found that ultrasound will accelerate a nonmetallic catalyst. Hydrosilation of acrylonitrile presents a challenge because the preferred site for silicon attack is the alpha carbon producing an unstable compound that has little synthetic utility. Beta silylation leads to a far more useful intermediate. A new catalyst was developed in our laboratories composed of Cu_2O and TMEDA that produces the desired beta adduct in very high

$$CH_2{=}CH{-}CN + H{-}SiCl_3 \xrightarrow[\text{TMEDA, }Cu_2O]{)))} Cl_3SCH_2{-}CH_2{-}CN$$

yield.[52] Contamination of the product mixture with the alpha isomer is <1%. Ultrasound greatly enhances the rate compared to stirring but optimum conditions call for refluxing for a short time. The results are summarized in Table VI. There are other examples of ultrasonically accelerated catalyses. Boudjouk and Han showed that palladium catalyzed hydrogenation of olefins and acetylenes using formic acid as the hydrogen source was

$$RCH{=}CH_2 + HCO_2H \xrightarrow{)))} RCH_2CH_3$$

improved considerably using ultrasound.[53] This method is very useful for small scale hydrogenations. The reactions are quick and the yields are essentially quantitative (Table VII).

Han has reported that the reduction of nitroaromatics using catalytic quantities of iron on carbon is enhanced by ultrasound[54]:

$$Ar{-}NO_2 + H_2NNH_2 \xrightarrow[Fe/C]{)))} Ar{-}NH_2\ (87{-}95\%)$$

$$Ar = H,\ p\text{-}MeO,\ p\text{-}NH_2,\ o\text{-}NO_2,\ p\text{-}NO_2$$

TABLE VI

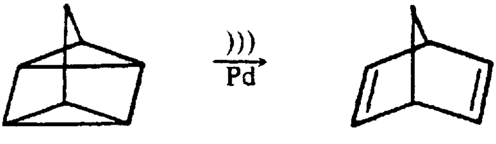
Hydrosilylation of acrylonitrile catalyzed by Cu_2O and tetramethylethylenediamine

Silane	Conditions[a]	Product	Yield,[b] %
$HSiCl_3$	10 min. reflux	$Cl_3SiCH_2CH_2CN$	95–100
$HSiCl_3$	2 h.)))	$Cl_3SiCH_2CH_2CN$	80
$HSiCl_3$	4 h. stir	$Cl_3SiCH_2CH_2CN$	30
$HSiMeCl_2$	45 min. reflux	$MeCl_2SiCH_2CH_2CN$	98–100
$HSiMeCl_2$	6 h.)))	$MeCl_2SiCH_2CH_2CN$	60
$HSiMeCl_2$	18 h. stir	$MeCl_2SiCH_2CH_2CN$	11
$HSiMe_2Cl$	24 h. reflux	no reaction	
$HSiMe_2Cl$	10 h.)))	no reaction	
$HSiMe_2Cl$	10 h. stir	no reaction	
$HSiPhCl_2$	30 min. reflux	$PhCl_2SiCH_2CH_2CN$	98–100
$HSiPhCl_2$	4 h.)))	$PhCl_2SiCH_2CH_2CN$	70–75
$HSiPhCl_2$	21 h. stir	$PhCl_2SiCH_2CH_2CN$	32
$HSiPh_2Cl$	24 h. reflux	$Ph_2ClSiCH_2CH_2CN$	5–10
$HSiPh_2Cl$	12 h.)))	no reaction	
$HSiPh_2Cl$	18 h. stir	no reaction	

[a] All reactions, except runs 1, 4, 7, 10, 13 were run at 30°C by using a 0.04:0.06:0.0069:0.019 mol ratio of acrylonitrile/silane Cu_2O/TMEDA, while reaction 1, 4, 7, 10 and 13 were run with 0.04:0.05:0.0069:0.019 mol ratios. All reactions were run in the absence of solvent.

[b] Yields are based on product isolated by distillation.

and Taoda has observed that that sonication accelerated the palladium catalyzed quadricyclane–norbornadiene rearrangement by almost a factor of ten.[55]



I

Activated metals. The synthetic utility of activated metals generated by alkali metal reduction of metal halides has been demonstrated by Rieke and co-workers.[56] Our contribution to this methodology has been to employ ultrasonic waves to modify the reduction process which normally calls for potassium and refluxing for several hours. Using an ultrasonic bath at or near room temperature, we

TABLE VII

Sonochemical synthesis of transition-metal carbonyl anions

Metal Carbonyl Anions		Yields[a] 4.4 atm CO	1 atm CO
$W_2(CO)_{10}^{2-}$	from WCl_6	47%	40%
$Mo_2(CO)_{10}^{2-}$	from $MoCl_5$	54%	39%
$Cr_2(CO)_{10}^{2-}$	from $CrCl_3$	7%	3%
$Ta(CO)_6^-$	from $TaCl_5$	6%	
$Nb(CO)_6^-$	from $NbCl_5$	51%	23%
$V(CO)_6^-$	from $VCl_3(THF)_3$	35%	23%

[a]Yields are based on metal halide and were calculated spectrophotometrically.

were able to reduce a wide variety of metal halides to metal powders in 10–40 minutes using lithium as the reducing metal.[57]

$$MX_n + nA \xrightarrow[\text{THF}]{)))} M^* + n\,AX$$

M = Main Group and Transition Metals
X = Cl, Br, I; A = Li, Na, K

The reactivities of some of these metal powders were far greater than commercial powders. Nickel and copper produced by this method, for example, were very efficient in the Ullman coupling of benzyl bromide[57]:

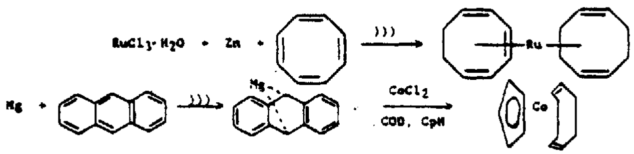
$$PhCH_2Br + Ni^* \text{ (or } Cu^*) \xrightarrow{)))} PhCH_2{-}CH_2Ph$$

and activated zinc made the Reformatsky reaction quantitative in a few minutes at room temperature[57]:

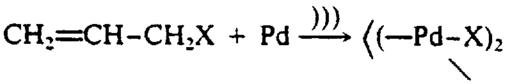
$$C_6H_5CHO + BrCH_2COOCH_2CH_3 + Zn^* \xrightarrow{)))} C_6H_5CH(OH)CH_2COOCH_2CH_3$$

Activated metals are also involved in Suslick's synthesis of metal carbonyl anions from sodium sand, metal halide and carbon monoxide.[58] These observations, which are summarized in Table VII, should be very useful for the synthesis of C-13 enriched salts.

Similarly, ultrasound-promoted reductions of metal halides led to improved routes to a ruthenium complex[59] and a cobalt complex[60]:



The formation of pi-allylic palladium complexes from allylic halides and palladium black under ultrasonic irradiation has also been reported (see Table VIII)[61]:



$$CH_2{=}CH{-}CH_2X + Pd \xrightarrow{)))} ((\text{—}Pd{-}X)_2$$

Nonmetals. While nonmetallic reagents are generally less responsive than metals towards ultrasonic waves, there is a growing list of synthetically important reactions involving nonmetals that are significantly enhanced by sonication. Metal hydrides, for example, which are used as bases and as reducing agents, have increased reactivity in the presence of ultrasonic waves. In 1966 Sjöberg reported that sodium hydride produced higher yields of the dimsyl anion from dimethylsulfoxide when the reaction mixture was sonicated[62]:

$$CH_3S(O)CH_3 + NaH \xrightarrow{)))} CH_3S(O)CH_2^- \, Na^+$$

TABLE VIII

Hydrogenation of carbon–carbon double bonds by formic acid catalyzed by palladium on carbon[a]

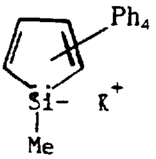
Olefin	Product	
$C_7H_{15}CH{=}CH_2$	C_9H_{20}	(100%)
		(95%)
trans-$PhCH{=}CHPh$	$PhCH_2CH_2Ph$	(100%)
$Ph{-}\underset{\underset{CH_3}{\vert}}{C}{=}CH_2$	$PhCH{-}CH_3$ $\diagdown CH_3$	(100%)
trans-$PhCH{=}CH{-}\overset{O}{C}{-}CH_3$	$PhCH_2CH_2\overset{O}{C}CH_3$	(100)
n-$C_4H_9OCH{=}CH_2$	*n*-$C_4H_9OC_2H_5$	(93%)
Methyl 9-octadecenoate	Methyl 9-octadecanoate	(90)

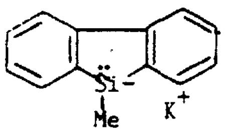
[a] Typical olefin:formic acid:catalyst mole ratios were 1:4:0.08.

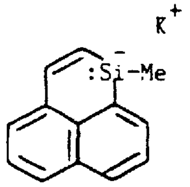
Boudjouk and Sooriyakumaran found that potassium hydride removed the hydrogen from a variety of silanes to form silyl anions in very high yields at room temperature with ultrasound.[63] The reaction is essentially quantitative for

$$\mathrm{RMe_2Si{-}H} + \mathrm{K{-}H} \xrightarrow{)))} \mathrm{RMe_2Si{:}^-\ K^+} + \mathrm{H_2}$$

vinyl and phenyl silanes allowing careful spectroscopic work. Using this methodology, it was possible to measure accurately the chemical shifts of three potentially aromatic silyl anions and their carbon analogues to demonstrate that the silyl anions were not aromatic.[63]







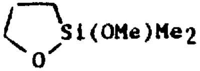
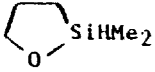
Lithium aluminum hydride is a far more efficient reducing agent of aryl halides when ultrasound is used.[64] Lukevics applied this methodology to silicon, germanium and tin functionals and found that ultrasound so activated the $LiAlH_4$ that it was an excellent reducing agent even in hydrocarbon solvents (Table IX).[65] The selective syntheses and relative reactivities of a variety of selenium dianion and diselenide dianion salts have been obtained because ultrasound permitted a convenient preparative route.[66] The mild conditions of the reaction allowed nearly quantitative production of either Se^{2-} or Se_2^{2-} by merely controlling the stoichiometry of the alkali metal and selenium (Table X). The relative reactivities of the dianions towards organic electrophiles were found to be $Li_2Se_2 \gg Na_2Se_2 \gg K_2Se_2 > K_2Se > Na_2Se > Li_2Se$.[64] Easy access to selenide dianions led to facile synthesis of organometallic selenides. Thus cyclosilselanes and cyclostannaselanes can be prepared in good yields[66]:

$$\mathrm{R_2MCl_2} + \mathrm{Na_2Se} \longrightarrow \mathrm{(R_2MSe)_3}\ 55\text{–}85\%$$

$$\mathrm{M = Si,\ Sn;\quad R = Me,\ Et,\ Ph}$$

TABLE IX

Ultrasonically promoted reduction of Group 14 functionals

Substrate	Solvent	Reaction time, h	Temperature, °C	Hydride[a]	Yield, % (by GLC)
Me_3SiCl	hexane	3	40	Me_3SiH	80[b]
Ph_2SiHCl	hexane	2	40	Ph_2SiH_2	>95
Et_3GeCl	pentane	4.5	40	Et_3GeH	>95
Me_3SnCl	cyclohexane	2.5	25	Me_3SnH	>95
Me_3SiNEt_2	hexane	3	40	Me_3SiH	70[b]
	pentane	3	25	 100	100

[a] 0.2 M solutions of substrate; $LiAlH_4$:substrate molar ratio = 3:1.
[b] Isolated yield.

TABLE X

Reductions of Se by K, Na, and Li in THF[a]

Reaction	Reduction Conditions	Time
I. $2K + 2Se \rightarrow K_2Se_2$	reflux	40 min
	ultrasound	85 min
	stir	150 min
II. $2K + Se \rightarrow K_2Se$	reflux	55 min
	ultrasound	120 min
	stir	300 min
IV. $2Na + 2SE \rightarrow Na_2Se_2$	reflux	65 min
	ultrasound	65 min
	stir	135 min
II. $2Na + Se \rightarrow Na_2Se$	reflux	80 min
	ultrasound	85 min
	stir	180 min
III. $2Li + 2Se \rightarrow Li_2Se_2$	reflux	8 h
	ultrasound	9.5 h
	stir	15 h
IV. $2Li + Se \rightarrow Li_2Se$	reflux	12 h

[a] Reductions performed in the presence of naphthalene (10 mol % with respect to the alkali metal). Ultrasound and stirring reactions were at 35–40°C.

Acknowledgments

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