refined by adjusting the frequencies so that the entropy change for the reaction

$$H_2O\cdot H_3O^+ \rightleftharpoons H_3O^+ + H_2O \qquad (A\text{-}1)$$

calculated using statistical thermodynamics matched the measured ΔS from equilibrium studies.[39] Finally the zero-point energy differences between $H_2O\cdot H_3O^+$ and $H_3O^+ + H_2O$ was calculated using statistical thermodynamics from known heats of formation,[40] the proton affinity of H_2O,[41] and the ΔH of reaction A-1 from equilibrium studies.[39]

Parameters for the CO_2 system were evaluated in a similar way to those for the water system. Vibrational frequencies and rotational constants of $CO_2^{+\cdot}$ and CO_2 are available from spectroscopic studies.[42] Since we could find no experimental or theoretical information on the structure of $CO_2\cdot CO_2^{+\cdot}$, we assumed that the CO_2 moieties are parallel with a C–C distance of 2 Å to calculate the rotational constant. The vibrational frequencies of $CO_2\cdot CO_2^{+\cdot}$ and the zero-point energy difference were evaluated as described above for $H_2O\cdot H_3O^+$ using the ΔS and ΔH recently measured by Headley et al.[5]

For $H_2O\cdot H_3O^+$ and $CO_2\cdot CO_2^{+\cdot}$ there are several reported measurements of ΔH and ΔS.[5,39,43,44] The ΔH values agree within 10%. The ΔS values show a larger scatter. Since the ΔS values were used to refine the vibrational frequencies of the complexes, some trial calculations were performed for $H_2O\cdot H_3O^+$ with the vibrational frequencies raised and lowered by 20% to determine how sensitive the calculations were to these parameters. Changing the vibrational frequencies over a range of 40% (which corresponds to a range in ΔS of 20%) resulted in a change of less than 20% in the calculated average kinetic energy release. The calculated average kinetic energy release increased as the vibrational frequencies were lowered. These changes could not account for the discrepancy between experiment and theory in the $H_2O\cdot H_3O^+$ systems, but changes of this magnitude could account for the smaller differences found between experiment and theory in the $CO_2\cdot CO_2^{+\cdot}$ system. For a 40% change in the vibrational frequencies the calculated metastable to main beam intensity ratio changed by a factor of approximately 2. The intensity ratio increased as the vibrational frequencies were lowered. Since in Figure 2 the log of the intensity ratio is plotted, changing the vibrational frequencies in the calculations is reflected as a relatively small offset to the calculated lines. This does not affect our conclusions regarding the operation of rear unit stabilization efficiencies in these systems. The calculated line is much more sensitive to the stabilization efficiency; reducing the stabilization efficiency to 0.5 results in nearly an order of magnitude increase in the calculated intensity ratio.

Registry No. $H_2O\cdot H_3O^+$, 22206-74-2; $NH_3\cdot NH_4^+$, 56044-48-5; $CO_2\cdot CO_2^+$, 12693-15-1.

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Sonochemistry and Sonocatalysis of Metal Carbonyls

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Abstract: Ultrasonic irradiation of liquids produces acoustic cavitation: the rapid formation, growth, and implosive collapse of vapor filled vacuoles. This generates short-lived "hot spots" with peak temperatures ~3000 K and nanosecond lifetimes. We have studied the effects of high intensity ultrasound on a variety of metal carbonyls and have observed the general phenomenon of sonochemical ligand dissociation, which often produces multiple CO substitution. $Fe(CO)_5$, for example, upon sonolysis, yields $Fe_3(CO)_{12}$ in the absence of additional ligands and $Fe(CO)_3L_2$ and $Fe(CO)_4L$ (L = phosphine or phosphite) in their presence. Similar substitution patterns are observed for $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. In all cases examined the rates of sonochemical ligand substitution are first order in metal carbonyl concentration and independent of L concentration. In addition, ln K_{obsd} correlates well with solvent system vapor pressure. These results are consistent with a dissociative mechanism in which coordinatively unsaturated species are produced by the cavitation process. Further use of these transient intermediates is made as alkene isomerization catalysts. Sonocatalysis by a wide range of metal carbonyls shows many similarities to photocatalysis, but different relative efficiencies and selectivities have also been observed.

The chemical effects of high intensity ultrasound arise from acoustic cavitation of liquids:[1] this rapid formation, growth, and implosive collapse of gas vacuoles generates short-lived (~ns), localized "hot spots" whose peak temperatures and pressures have been measured at ~3000 K and ~300 atm,[2] confirming earlier calculations.[3] Analogies to flash pyrolysis, photochemistry, radiolysis, and other high-energy processes can be made. A resurgence of interest in the chemical uses of ultrasound in homogeneous[4,5] and heterogeneous[6] systems may be noted. We

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Table I. Sonochemical Clusterification of $Fe(CO)_5$

system[a]	d[$Fe_3(CO)_{12}$]/d*t*, mM/h	d[Fe]/d*t*, mmol/h	rel yield[b] of $Fe_3(CO)_{12}$, %
neat $Fe(CO)_5$	1.59	1.19	3.8
0.77 M $Fe(CO)_5$ in decalin	1.27	2.45	1.5
0.10 M $Fe(CO)_5$ in decalin	1.11	0.68	4.7
0.10 M $Fe(CO)_5$ in decane	0.45	0.55	2.4
0.10 M $Fe(CO)_5$ in octane	0.32	0.13	6.9
0.10 M $Fe(CO)_5$ in 0.5 M heptane in decalin	0.54	0.15	9.8
0.10 M $Fe(CO)_5$ in heptane	0.15	<0.001[c]	>82

[a] 0 °C, 20 kHz, ~150 W/cm^2, 10-mL volume, under Ar atmosphere. [b] Based on equivalents of Fe. [c] None detected.

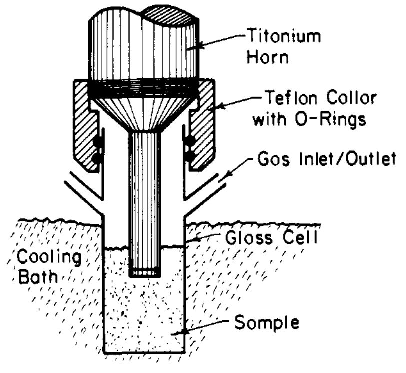

Figure 1. Inert-atmosphere sonication reactor.

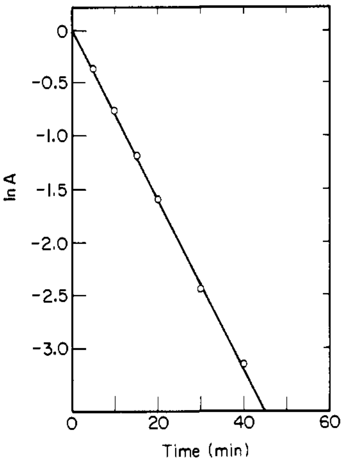

Figure 2. First-order kinetics of the sonolysis of $Fe(CO)_5$. Absorbance at 1999 cm^{-1} utilized. The observed rate constant in decalin at 21 °C is 1.34×10^{-3} s^{-1}; $\tau_{1/2} = 8.6$ min.

recently reported the first observation of the sonochemistry of metal carbonyls and the use of ultrasound to initiate homogeneous catalysis[4a] and present the extension of that work here.

Our goal in this effort is to explore the chemical effects of high intensity ultrasound on well-defined systems whose thermal and photochemical reactivities are well understood. The transition-metal carbonyls make an excellent choice for these initial studies. For example, thermolysis of $Fe(CO)_5$ above 100 °C gives pyrophoric, finely divided iron powder;[7] ultraviolet photolysis[8] yields $Fe_2(CO)_9$, via the intermediacy of $Fe(CO)_4$; multiple infrared photolysis in the gas phase[9] yields isolated Fe atoms. Multiple ligand dissociation, generating $Fe(CO)_3$, $Fe(CO)_2$, etc., is not available from ordinary thermal or photochemical processes but can occur in low-temperature inert matrices[10] and with gas-phase laser photolysis.[11] These observations underline the dual difficulties inherent in creating controlled multiple ligand dissociation: first, to deliver sufficient energy in a utilizable form and, second, to quench the highly energetic intermediates before complete ligand loss occurs.

Another aspect of our interest in organometallic sonochemistry is the initiation of homogeneous catalysis by ultrasonic irradiation. Again, metal carbonyls are excellent trial systems, since their use as catalysts for a wide variety of transformations has been extensively studied.[12] Of special interest here is the isomerization of terminal to internal olefins by either thermal[13] or photochemical[14] activation of metal carbonyls.

Experimental Section

All ultrasonic irradiations were made with collimated 20-KHz beam from a lead zirconate titanate transducer with titanium amplifying horn (Heat-Systems Ultrasonics, Inc., Model W375-P) directly immersed in the solution. The reactions were performed in a glass sonication cell under an Ar atmosphere, as illustrated in Figure 1. Typical sonication volumes were 10 mL, but cells as large as 200 mL have been used. Sonications must be made under conditions of low solvent volatility. If the vapor pressure of the system is large, effective compression of the cavities does not occur, and the local heating is lost.[4b] Temperature control was provided with a refrigerated constant temperature bath, and actual temperatures during sonication were measured by thermocouple held in the middle of the sonication cell free from contact with either walls or horn.

Solvents were spectrophotometric or reagent grade and purified in the usual ways.[15] Iron pentacarbonyl was obtained from Alfa-Ventron, distilled or filtered before use, and stored at −30 °C under Ar in the dark.

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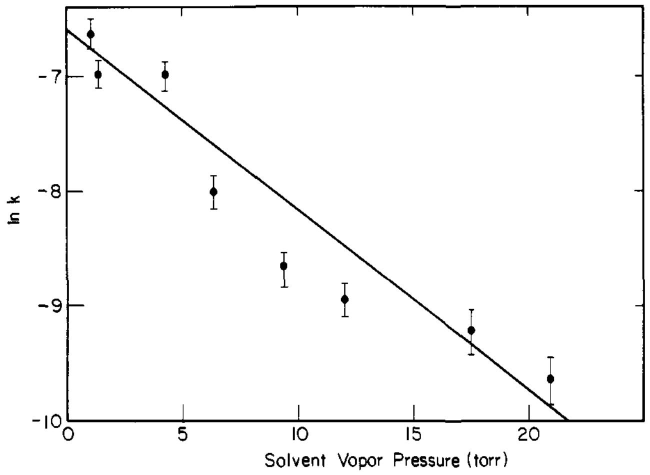

Figure 3. First-order rate constant (s^{-1}) for sonolysis of $\mathrm{Fe(CO)_5}$ vs. solvent vapor pressure at 25 °C. In order of increasing vapor pressure: decalin, decane, nonane, 0.22 mol fraction of octane in nonane, 0.52 mol fraction of octane in nonane, octane, 0.11 mol fraction of heptane in octane, 0.22 mol fraction of heptane in octane. Vapor pressures calculated from data in ref 25, assuming ideal solution behavior.

Triiron dodecacarbonyl was obtained from Alfa-Ventron, purified by hexane–Soxhlet extraction, and stored at −30 °C under Ar in the dark. Other metal carbonyls were used as received from Alfa-Ventron. Triphenylphosphine, obtained from Aldrich, was recrystallized from ethanol. Trimethyl phosphite and triethyl phosphite, obtained from Aldrich, were run through an alumina column and distilled from Na. Other phosphines and phosphites were used as supplied from Aldrich.

Infrared analysis utilized Nicolet 7199 and MX-5 Fourier transform infrared spectrophotometers. Quantitative analysis relied on measured extinction coefficients and are accurate to ±10%. Vapor-phase chromatography was performed on a Varian 3700 gas chromatograph, equipped with capillary column injector and flame ionization detectors on a 50-m OV-101 fused silica capillary column, interfaced to a Hewlett-Packard 3380 reporting integrator. UV–vis spectra were obtained on a Hitachi 100-80 spectrophotometer in matched quartz cells.

In a typical experiment, a 10-mL solution would be deoxygenated by argon flush and transferred by cannula to the sonication cell which was then allowed to reach temperature equilibrium with the cooling bath. During ultrasonic irradiation, an initial temperature rise was observed by thermocouple probe with a steady-state temperature reached within 5 min. Small aliquots were removed during the course of the reaction for analysis. Thermal controls were run under identical conditions but at temperatures >10 °C warmer than those observed during irradiation.

Results and Discussion

Clusterification. Sonication of $\mathrm{Fe(CO)_5}$, neat or in alkane solutions, yields $\mathrm{Fe_3(CO)_{12}}$ and finely divided iron, as shown in Table I. As shown in Figure 2, the rate of decomposition of $\mathrm{Fe(CO)_5}$ is first order in $[\mathrm{Fe(CO)_5}]$ over greater than 4 half-lives. This is consistent with a simple dissociative process activated by the intense local heating generated by acoustic cavitation. Further evidence for this "hot spot" mechanism comes from the effect of solvent vapor pressure on the rate of $\mathrm{Fe(CO)_5}$ sonolysis. When a transient cavity is filled with a large vapor pressure, compression by the sound field will first create recondensation rather than adiabatic heating; in addition the high-vapor content allows thermal transport during collapse, which diminishes the local heating even further.[3] Thus, as the vapor pressure of the solvent system increases, the intensity of the cavitational collapse and the maximum temperature reached during such collapse will decrease. As we have noted elsewhere,[4b,c] a rough correlation between log (sonochemical rate) and vapor pressure is expected. We show in Figure 3 the correlation between the log of the first-order rate constant of the decomposition of $\mathrm{Fe(CO)_5}$ and the solvent vapor pressure.

The mechanism by which $\mathrm{Fe_3(CO)_{12}}$ is formed during sonolysis of $\mathrm{Fe(CO)_5}$ does not involve $\mathrm{Fe_2(CO)_9}$ as an intermediate. Sonication of $\mathrm{Fe_2(CO)_9}$ does not produce $\mathrm{Fe_3(CO)_{12}}$ but rather $\mathrm{Fe(CO)_5}$ and finely divided iron at rates fast compared to $\mathrm{Fe_3(CO)_{12}}$ production from $\mathrm{Fe(CO)_5}$ sonication. Direct sonication of $\mathrm{Fe_3(CO)_{12}}$ does not produce decomposition at detectable rates: neither declusterification nor formation of iron occurs even after exhaustive sonication in alkanes in the absence of ligands.

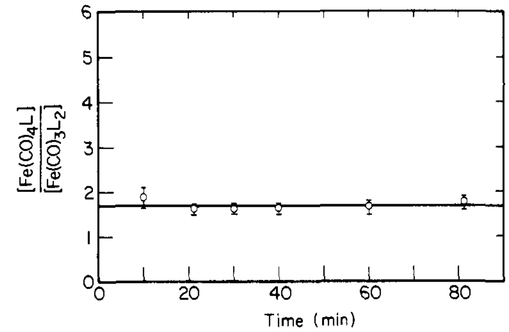

Figure 4. Sonochemical ligand substitution of $\mathrm{Fe(CO)_5}$ with $\mathrm{P(C_6H_5)_3}$. $[\mathrm{Fe(CO)_5}] = 7.3$ mM and $[\mathrm{P(C_6H_5)_3}] = 75$ mM in nonane at 21 °C.

The production of $\mathrm{Fe_3(CO)_{12}}$ arises from initial dissociative loss of CO from the cavitational heating of $\mathrm{Fe(CO)_5}$, as in eq 1,[16]

$$\mathrm{Fe(CO)_5}\ {-)))}\!\!\rightarrow \mathrm{Fe(CO)_{5-\mathit{n}}} + n\mathrm{CO}\ (n = 1\text{–}5) \tag{1}$$

$$\mathrm{Fe(CO)_3} + \mathrm{Fe(CO)_5} \rightarrow \mathrm{Fe_2(CO)_8} \tag{2}$$

$$2\mathrm{Fe(CO)_4} \rightarrow \mathrm{Fe_2(CO)_8} \tag{3}$$

$$\mathrm{Fe_2(CO)_8} + \mathrm{Fe(CO)_5} \rightarrow \mathrm{Fe_3(CO)_{12}} + \mathrm{CO} \tag{4}$$

followed by secondary reactions with excess $\mathrm{Fe(CO)_5}$. On the basis of ligand-trapping studies, we favor the sonochemical production of $\mathrm{Fe(CO)_3}$ and reaction with $\mathrm{Fe(CO)_5}$, as in eq 2, but cannot rule our the dimerization of $\mathrm{Fe(CO)_4}$ in the localized cavitation site, as shown in eq 3. The reaction of $\mathrm{Fe_2(CO)_8}$ with $\mathrm{Fe(CO)_5}$ may proceed through initial dissociation to form $\mathrm{Fe_2(CO)_7}$, by analogy to the photochemistry of $\mathrm{Fe(C_4H_4)(CO)_3}$ which produces $\mathrm{Fe_2(C_4H_4)_2(CO)_3}$ in frozen matrices.[17]

As shown in Table I, we may alter the ratio of observed products over a 100-fold range simply by altering the solvent vapor pressure. As the vapor pressure increases, the peak temperature reached during cavitational collapse diminishes, as noted earlier. Our results argue, therefore, that the sonochemical production of metallic iron requires a higher activation than does the production of $\mathrm{Fe_3(CO)_{12}}$, as one would expect.

Ligand Substitution. In addition to clusterification, sonochemical ligand substitution also occurs for $\mathrm{Fe(CO)_5}$ and in fact for most metal carbonyls. Sonication of $\mathrm{Fe(CO)_5}$ in the presence of phosphines or phosphites in various alkanes produces $\mathrm{Fe(CO)_4L}$, $\mathrm{Fe(CO)_3L_2}$, and small amounts of $\mathrm{Fe(CO)_2L_3}$[20] and, with low vapor pressure solvents only, finely divided Fe. This reaction has been used as a mechanistic probe of photochemical reaction,[8,17] and we have extended its use here. As shown in Figure 4, the ratio of $[\mathrm{Fe(CO)_4L}]/[\mathrm{Fe(CO)_3L_2}]$ does not change with length of sonication. In keeping with this, we find that $\mathrm{Fe(CO)_4L}$ is *not*

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[16] The symbol $-)))\!\!\rightarrow$ is used to represent ultrasonic irradiation.

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[18] (a) Analyses were performed by quantitative FTIR; cf. ref 19. (b) The ligand-trapping evidence for multiplying coordinately unsaturated intermediates is not completely conclusive in sonolysis of $\mathrm{Fe(CO)_5}$, however, because any $\mathrm{Fe_2(CO)_9}$ transiently produced will thermally react with phosphines to yield $\mathrm{Fe(CO)_3L_2}$ and $\mathrm{Fe(CO)_4L}$.[20] This appears to us to explain the small amounts of $\mathrm{Fe(CO)_3L_2}$ produced by photolysis[8] of $\mathrm{Fe(CO)_5}$ in the presence of L. However, this cannot be the case for substitution of $\mathrm{Cr(CO)_6}$, which does not form clusters but which still shows multiple substitution as a primary product of sonolysis but not as an initial photochemical or thermal product.

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[20] (a) Manuel, T. A. *Adv. Organomet. Chem.* **1966**, *3*, 181. (b) We find that $\mathrm{Fe(CO)_4L}$ is sonochemically converted to finely divided iron but at rates much slower (less than 10%) than those of the sonochemical substitution of $\mathrm{Fe(CO)_5}$. The sonochemical stability of $\mathrm{Fe(CO)_4L}$ is dominated by the steric bulk of L. In nonane sonolysis of $\mathrm{Fe(CO)_4L}$, for L = $\mathrm{P(OCH_3)_3}$, $\mathrm{P(OC_2H_5)_3}$, $\mathrm{P(OCH_2CH_2CH_2CH_3)_3}$, and $\mathrm{P(C_6H_5)_3}$ the k_{obsd} ($s^{-1} \times 10^5$) are 1.2, 6.7, 8.0, and 9.0, respectively.

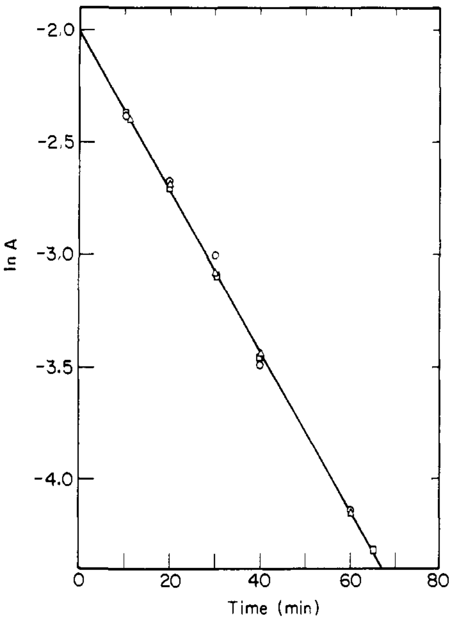

Figure 5. First-order kinetics of sonochemical ligand substitution. $[Fe(CO)_5]$ = 1.21 mM in nonane at 21 °C; $[P(OMe)_3]$ = 1.13 mM (□), 11.9 mM (△), and 36.5 mM (○). First-order rate constant is 6.0×10^{-4} s^{-1}; $\tau_{1/2}$ = 19.4 min.

sonochemically converted to $Fe(CO)_3L_2$ even in the presence of high [L] [20b] Furthermore, the rate of sonolysis of $Fe(CO)_5$ in the presence of L is first order in $[Fe(CO)_5]$ and *independent* of [L], as shown in Figure 5. The ratio of $Fe(CO)_4L$ to $Fe(CO)_3L_2$ produced, moreover, decreases with increasing [L].[18a] These observations are consistent with the general mechanism shown in Scheme I.[18b]

Scheme I

$$\mathrm{Fe(CO)_5} \;{-})))\!\!\rightarrow\; \mathrm{Fe(CO)}_{5-n} + n\mathrm{CO} \tag{5}$$

$$\mathrm{Fe(CO)_4 + L \rightarrow Fe(CO)_4L} \tag{6}$$

$$\mathrm{Fe(CO)_3 + L \rightarrow Fe(CO)_3L} \tag{7}$$

$$\mathrm{Fe(CO)_3L + CO \rightarrow Fe(CO)_4L} \tag{8}$$

$$\mathrm{Fe(CO)_3L + L \rightarrow Fe(CO)_3L_2} \tag{9}$$

$$\mathrm{Fe(CO)_4L + L} \;{-})))\!\!\rightarrow\; \mathrm{Fe(CO)_3L_2} \tag{10}$$

Sonochemical ligand substitution of $Fe_3(CO)_{12}$ also occurs. Yields are quantitative for $Fe(CO)_4L$ and $Fe(CO)_3L_2$; their ratio is dependent on L and its concentration. For $P(C_6H_5)_3$ in large excess, the limiting ratio of $[Fe(CO)_4L]/[Fe(CO)_3L_2]$ produced is 1.1. The sonochemical substitution occurs readily even at −20 °C in various alkanes. In comparison to thermal substitution under these conditions,[21a] ultrasound accelerates the rate of substitution $\gg 10^3$. Thermal substitution occurs readily at higher temperatures but shows induction periods of several hours before formation of $Fe(CO)_3L_2$ and $Fe(CO)_4L$ occurs.[21a] We believe this is due to the intermediacy of $Fe_3(CO)_{11}L$, which has been isolated as one of the thermolysis products.[21b] In addition, $Fe(CO)_4L$ is rapidly thermally substituted to yield $Fe(CO)_3L_2$, the sole product observed[21c] in the presence of excess L. The photochemical substitution[8] of $Fe_3(CO)_{12}$ yields these same products but with relative efficiencies of ~1:100 compared to $Fe(CO)_5$. In contrast, sonochemical substitutions of $Fe_3(CO)_{12}$ compared to $Fe(CO)_5$ have rates that are ~10:1. Since $Fe_3(CO)_{12}$ is sonochemically inert in the *absence* of added ligands, we speculate that the cavitational hot spot generates an intermediate which can rapidly return to $Fe_3(CO)_{12}$ unless trapped by added ligands (one such possibility is a ring-opened metallodiradical like that suggested[14e] in the photochemistry of $Ru_3(CO)_{12}$).

Table II. Sonocatalysis of 1-Pentene Isomerization by Iron Carbonyls

precatalyst[a] (amount, M)	length of sonication, h	av rate of 2-pentene formation, M/h	initial turnover rate[c]
$Fe(CO)_5$ (0.01)	1	1.5×10^{-1}	17
$Fe(CO)_5$ (0.1)	1	2.0×10^{-1}	4
$Fe(CO)_5$ (0.1)	0[b]	$<1 \times 10^{-6}$	$<10^{-5}$
$Fe_2(CO)_9$ (0.01[d])	1	1.7×10^{-1}	51
$Fe_2(CO)_9$ (0.01[d])	0[b]	$<2 \times 10^{-4}$	$<2 \times 10^{-2}$
$Fe_3(CO)_{12}$ (0.001)	1	7.1×10^{-3}	86
$Fe_3(CO)_{12}$ (0.01[d])	1	1.3×10^{-2}	15
$Fe_3(CO)_{12}$ (0.01[d])	0[b]	$<2 \times 10^{-4}$	$<2 \times 10^{-2}$
none	1	$<2 \times 10^{-4}$	

[a] 0.5 M 1-pentene in decane, $T = 0$ °C, ~100 W/cm², 10-mL volume, under Ar atmosphere; similar results are observed in toluene, heptane, and di-*n*-butyl ether. [b] Controls were run under identical conditions for ⩾60 min but without ultrasonic irradiation. *No 2-pentene was observable* (<0.05% of 1-pentene) under these conditions. [c] Initial turnover rates during sonication have been calculated as mol of 1-pentene isomerized/mol of precatalyst/h, as determined during the first 5 min of sonication. [d] Undissolved precatalyst is present.

Sonochemical ligand substitution occurs with other metal carbonyls as well. At 10 °C, $Cr(CO)_6$ readily produces upon sonolysis $Cr(CO)_5L$, $Cr(CO)_4L_2$, and in small amounts $Cr(CO)_3L_3$, where L = $P(OCH_3)_3$ or $P(C_6H_5)_3$, though in lower yields than the iron carbonyls. The rate of substitution is first order in $[Cr(CO)_6]$, independent of [L], and, depending on conditions, $k_{obsd} \approx 5 \times 10^{-4}$ s^{-1}, with the ratio of $[Cr(CO)_4L_2]/[Cr(CO)_5L]$ quite high (>4). As in the $Fe(CO)_5$ case, this ratio is independent of length of sonication, and $Cr(CO)_5L$ is not sonochemically substituted at appreciable rates. The multiple ligand substitution of $Cr(CO)_6$, then, must be due to multiple loss of CO during the acoustic cavitation event. In this system where clusters do not form, we have unambiguous evidence for the formation of multiply coordinatively unsaturated species by sonolysis.

$Mo(CO)_6$ and $W(CO)_6$ also undergo analogous sonochemical substitution, yielding $M(CO)_5L$ and $M(CO)_4L_2$, but at rates that are fivefold and 13-fold slower, respectively, than that for $Cr(CO)_6$. This is in contrast to the rates of thermal substitution[22a] (Mo > Cr > W) but does parallel the *average* M–CO bond strengths.[22b] It is more likely, however, that the sonochemical reactivity reflects the relative concentrations of the metal carbonyls in the vapor phase of the cavitation event. For $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, the reported[22a] heats of sublimation are 71.6, 73.6, and 76.6 kJ/mol, respectively, and the extrapolated vapor pressures at 10 °C are 0.053, 0.036, and 0.006 torr, respectively.[22c,d] Substitution also occurs sonochemically with $Mn_2(CO)_{10}$, producing $Mn_2(CO)_8L_2$, and is discussed elsewhere.[4d] Thus, sonochemical ligand substitution is a general phenomenon among metal carbonyls. Furthermore, in several cases, multiple ligand substitution occurs via the intermediacy of multiply coordinatively unsaturated species. We have been able to do sonolysis at temperatures as low as 200 K, and experiments are underway to thermally trap such intermediates for spectroscopic characterization.

Sonocatalysis. The transient coordinatively unsaturated species produced from sonolysis of metal carbonyls are likely candidates for homogeneous catalysts, since similar species produced photochemically are among the most active catalysts known.[14] Sonication of $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ in 1-pentene solution produces *trans*- and *cis*-2-pentene in approximately a 3.5:1 ratio (i.e. the thermodynamic ratio[14g]), as shown in Table II. Useable

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Table III. Sonocatalysis of 1-Alkenes by $Fe(CO)_5$

alkene substrate[a]	products	rel rate[b]
1-pentene	*trans*-2-pentene (77%) *cis*-2-pentene (23%)	1.0
1-hexene	*trans*-2-hexene (74%) *cis*-2-hexene (26%)	1.1
2-ethylpent-1-ene	2-ethylpent-2-ene	0.31
1-octene	*cis*- and *trans*-2-octene	0.17
1-decene	*cis*- and *trans*-2-decene	<0.05
allylbenzene	β-methylstyrene	<0.02[c]
cis-stilbene	*trans*-stilbene	<0.02[c]

[a] [Alkene] = 0.50 M, [$Fe(CO)_5$] = 0.01 M in decane, 10 °C, under Ar, 44-W acoustic power. [b] Relative rates based on isomerization over 1-h sonication; estimated errors ±20%; absolute rates dependent on configuration used for irradiation. [c] No isomerization detected.

solvents that support this sonocatalysis include, in order of increasing observed rates of isomerization, toluene, tetrahydrofuran, diisopropyl ether, heptane, octane, decalin, decane, and di-*n*-butyl ether. The relative rates only vary by a factor of 5 over this set; roughly the trend parallels the vapor pressures of (and hence the cavitational intensity in) the solvent system.

For $Fe(CO)_5$, isomerization of 1-pentene is roughly linear for 60 min and continues for several hours before activity is gradually lost as finely divided Fe and small amounts of $Fe_3(CO)_{12}$ are produced. $Fe_2(CO)_9$ shows greater initial activity, which is lost as the $Fe_2(CO)_9$ is rapidly sonochemically converted to $Fe(CO)_5$. $Fe_3(CO)_{12}$ also shows high initial activity that diminishes during the sonication. In this case, however, no iron species other than $Fe_3(CO)_{12}$ are detected even after prolonged sonication. Purification of $Fe_3(CO)_{12}$ by sublimation or Soxhlet extraction does not change the observed sonocatalysis. As shown in Table II, the rate of 1-pentene isomerization can be enhanced by $>10^5$ by ultrasonic irradiation of the iron carbonyls, compared to the controls.

We have further investigated the range of substrates for sonocatalytic isomerization, as shown in Table III. Other terminal alkenes are readily isomerized, although increasing steric hindrance, as in 2-ethylpent-1-ene and allylbenzene, diminishes the observed rates. Notably *cis*-stilbene isomerization is not observed, due either to its lack of β-hydrogens or its steric bulk.

Extensions of ultrasonic activation of other metal carbonyls are shown in Table IV. Note that all the iron carbonyls produce *cis*- and *trans*-2-pentene in roughly the thermodynamic ratio, as expected if the same catalytic species were active. On the other hand, $Ru(CO)_5$ and $Ru_3(CO)_{12}$ produce very different trans/cis ratios demonstrating different catalytic species and suggestive of intact cluster catalysis by $Ru_3(CO)_{12}$. Comparison to photocatalytic isomerization by these metal carbonyls reveals some significant differences. The relative sonocatalytic activity decreases in the order $Ru_3(CO)_{12} > Fe(CO)_5 > Mo(CO)_6 > Fe_3(CO)_{12} \gg W(CO)_6 \approx Cr(CO)_6$; the photocatalytic activity[14a,e,g,h] yields $Fe(CO)_5 > Fe_3(CO)_{12} > Ru_3(CO)_{12} > W(CO)_6 \approx Mo(CO)_6 \gg Cr(CO)_6$. Furthermore, the trans/cis ratios are very different for sonocatalysis vs. photocatalysis[14a,e] by $Ru_3(CO)_{12}$ (2.8 vs. 6) but quite similar in all other cases. These results demonstrate that the catalytic species produced sonochemically from $Ru_3(CO)_{12}$ is *not* that produced photochemically and is relatively more active. The exact nature of these catalytic species remains unknown at present. Results are consistent with the generally accepted mechanism in analogous photocatalysis and thermal catalysis[13,14] of β-hydrogen migration and the intermediacy of a hydrido π-allyl complex. In keeping with this scheme, sonication of $Fe(CO)_5$ in the presence of excess 1-pentene does produce $Fe(CO)_4$(pentene), as determined from its infrared spectrum[14g] after spectral stripping by FTIR.

Table IV. Sonocatalysis of 1-Pentene Isomerization by Various Metal Carbonyls

precatalyst[a]	rel rate[b]	*trans*/*cis*-2-pentene[c]
$Fe(CO)_5$	1.0	3.6
$Fe_2(CO)_9$[d]	1.1	3.6
$Fe_3(CO)_{12}$[d]	0.09	3.1
$Ru(CO)_5$[e]	1.2	4.0
$Ru_3(CO)_{12}$	2.4	2.8
$Cr(CO)_6$	<0.02	
$Mo(CO)_6$	0.41	1.8
$W(CO)_6$	<0.02	
$Co_2(CO)_8$	0.10	

[a] [1-Pentene] = 0.50 M, [precatalyst] = 0.01 M, in decane, 10 °C, under Ar, 44-W acoustic power. [b] Relative rates based on isomerization over 1-h sonication; estimated errors, ±20%; absolute rates dependent on configuration used for irradiation. [c] Trans/cis ratios ±10%; determined after <5% total conversion. In all cases, control experiments with no sonication produced no detectable 2-pentene. The equilibrium value[13c] for trans/cis ratio is 3.8. [d] Undissolved precatalyst initially present. [e] Produced by photolysis under CO.[23]

Conclusions. Ultrasonic cavitation creates extremely intense thermal heating but for only very brief duration. This can produce unusual chemistry, distinct from both photochemical and thermal processes. We have observed the general phenomenon of sonochemical ligand substitution of metal carbonyls, which often produces multiple CO substitution through the intermediacy of multiply coordinatively unsaturated species. In addition, the use of high-intensity ultrasound to initiate ligand dissociation is a novel method of catalyst activation with unique potential. The ability to induce ligand dissociation from complexes inert to photochemical or low-energy (<200 °C) thermal processes suggests that sonocatalysis may be produced by intermediates not normally accessible. Examples of such unusual chemistry include hydrocarbon activation under mild ambient conditions.[4c,24]

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