

The Sonochemistry of Some Metal Carbonyl Complexes

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Final Seminar

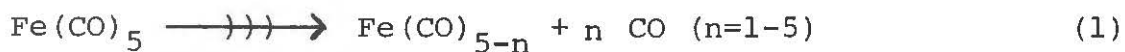
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Ultrasonic irradiation of solutions gives rise to a variety of effects including emulsification, ultrasonic cleaning, sonoluminescence, and chemical reactions [1,2]. The chemical action of ultrasound was first recognized in 1927 by Richards and Loomis [3], and is not due to a direct interaction between the sound and molecules, but to a phenomenon associated with it called acoustic cavitation [4]. This is the formation, growth, and collapse of gas bubbles in solution due to the action of the positive and negative pressure waves of the sound on the bubbles. During collapse of the cavities, temperatures of about 3000 K and pressures of about 300 atmospheres are reached within the bubble [5]. The primary goals of this research have been: to establish the ability of organic solvents to support sonochemical reactions with appreciable rates; to determine whether cavitation phenomena could induce sonochemical ligand dissociation and ligand substitution; and to determine whether the high temperatures and pressures attained within the cavity upon collapse could produce catalytic reactions normally performed only at elevated temperatures and pressures.

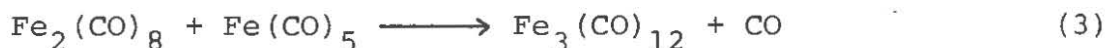
All sonications were performed using a Heat Systems-Ultrasonics model W375 Sonicator cell disruptor, which consists of a 20 kHz high voltage generator rated at 375 watts and a lead zirconate-titanate piezoelectric transducer driving a titanium amplifying horn. The sonicator was used primarily in the immersion tip configuration with the probe inserted into the solution. The reaction temperature was controlled using a constant temperature bath.

The majority of sonochemical reactions have been in aqueous solution [1,2] and it has generally been assumed that they "do not take place in pure organic liquids" [6]. Thus it was necessary to establish that sonochemistry did occur in a wide range of organic solvents. The reaction chosen for study was the bleaching of the stable free radical diphenylpicrylhydrazyl (DPPH), which is a standard free radical trap [7]. Bleaching of DPPH was observed in all of the solvents attempted, indicating that these liquids will support sonochemical reactions. Further work in our group [8] found that the primary factor influencing the extent of cavitation, and thus the rate of DPPH bleaching, is the vapor pressure of the solvent.

The iron carbonyls were chosen as the initial metal carbonyl for study because of their well studied thermal and photochemical reactivities [9,10,11]. Sonication of $\text{Fe}(\text{CO})_5$, neat or in hydrocarbon solvents, yields $\text{Fe}_3(\text{CO})_{12}$ and finely divided pyrophoric iron. The primary process induced by sonication may be described by reaction 1.

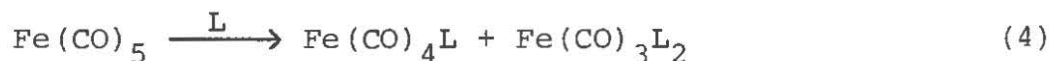


Production of $\text{Fe}_3(\text{CO})_{12}$ probably results from initial sonochemical production of $\text{Fe}(\text{CO})_3$, which may then react according to reactions 2 and 3



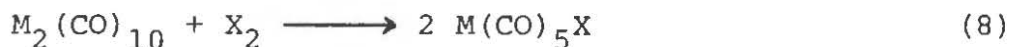
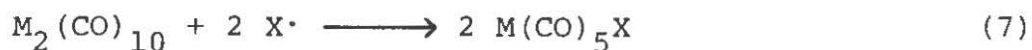
Another possible mechanism would produce $\text{Fe}_2(\text{CO})_8$ through dimerization of $\text{Fe}(\text{CO})_4$. The metallic iron produced may be due to initial loss of all carbonyls or spontaneous loss of CO from clusterification of $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})$.

In the presence of phosphorus donor ligands, L, $\text{Fe}(\text{CO})_5$ undergoes thermal, photochemical, and sonochemical substitution to yield a mixture of mono- and disubstituted iron carbonyls as shown below.



The thermal and photochemical reactions both proceed through initial substitution of one CO, giving $\text{Fe}(\text{CO})_4\text{L}$, which then undergoes a second substitution to give $\text{Fe}(\text{CO})_3\text{L}_2$. In the ultrasonic substitution both $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$ are formed simultaneously, and $\text{Fe}(\text{CO})_4\text{L}$ does not yield $\text{Fe}(\text{CO})_3\text{L}_2$ when sonicated in the presence of L. This again suggests the formation of $\text{Fe}(\text{CO})_3$ in the cavitation space. The sonochemical substitution of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ proceed in a similar manner, producing $\text{M}(\text{CO})_4\text{L}_2$ and $\text{M}(\text{CO})_5\text{L}$ simultaneously. Sonication of $\text{M}(\text{CO})_5\text{L}$ in the presence of phosphines again does not produce any disubstituted products.

The considerable recent interest [12,13,14,15] in the substitution reactions of the Group VIIB metal carbonyls led us to investigate their sonochemical reactions. Sonication of $\text{M}_2(\text{CO})_{10}$ ($\text{M}=\text{Mn}, \text{Re}$) in CCl_4 , CHCl_3 , CHBr_3 , and $\text{CHBr}_2\text{CHBr}_2$ yields $\text{M}(\text{CO})_5\text{X}$ in high yield. Unlike the photochemical reaction [16], sonication of $\text{M}_2(\text{CO})_{10}$ in benzyl chloride does not yield $\text{M}(\text{CO})_5\text{Cl}$. This suggests that the sonochemical route to $\text{M}(\text{CO})_5\text{X}$ does not involve initial metal-metal bond cleavage. Furthermore, the rate of reaction is independent of the metal carbonyl concentration. We propose the following mechanism for $\text{M}(\text{CO})_5\text{X}$ production.



Sonication of $\text{Mn}_2(\text{CO})_{10}$ in the presence of phosphines and phosphites produces $\text{Mn}_2(\text{CO})_8\text{L}_2$. Both $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$ fail to react sonochemically with these ligands. In addition, sonication of $\text{Mn}_2(\text{CO})_{10}$ with $\text{Re}_2(\text{CO})_{10}$ does not yield $\text{MnRe}(\text{CO})_{10}$ nor does the reverse reaction

occur sonochemically. Probable explanations for the behavior of $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$ are that cavitation heating is insufficient to break the stronger metal-metal bond in these species, or that their volatility is too low for them to be in significant concentration within the cavitation space, and thus they cannot undergo substitution.

Homogeneous hydrogenation of CO is typically performed [17,18,19] at temperatures of 200-300°C and pressures of from 200-1500 atmospheres. Since cavitation produces high local temperatures and pressures, experiments to determine whether sonication of CO and H_2 in the presence of $\text{Co}_2(\text{CO})_8$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ would produce any hydrocarbons upon sonication at 1 atmosphere. Sonication of CO and H_2 in sulfolane, THF, and N-methylpyrrolidine all yielded CH_4 and CH_3OH at average rates of 20 and 4.5 $\mu\text{M}/\text{min}$ respectively. Sonication in the presence of $\text{Ru}_3(\text{CO})_{12}$ with or without iodide promoters, rhodium (from $\text{Rh}_6(\text{CO})_{16}$ or $\text{Rh}_2(\text{CO})_4\text{Cl}_2$) with or without sodium or cesium promoters, $\text{Os}_3(\text{CO})_{12}$, or $\text{Co}_2(\text{CO})_8$ gave no additional hydrocarbon production. The IR of the $\text{Ru}_3(\text{CO})_{12}$ solution after sonication under H_2 and CO indicated formation of $\text{Ru}(\text{CO})_5$. $\text{Ru}(\text{CO})_5$ was not produced at appreciable rates in the presence of CO or H_2 alone. In a similar manner, sonication of $\text{Os}_3(\text{CO})_{12}$ under H_2 and CO slowly produced $\text{Os}(\text{CO})_5$. Under CO and hydrogen, $\text{Co}_2(\text{CO})_8$ reacted to give the clusters $\mu^3\text{-CH}[\text{Co}(\text{CO})_3]_3$ and $\text{Co}_4(\text{CO})_{12}$, plus an intractable solid. When this reaction was carried out under Ar its rate increased several fold.

This research has demonstrated that ligand dissociation and substitution of metal carbonyls may be brought about sonochemically, and that multiple simultaneous CO dissociation is likely in the case of iron and chromium carbonyls. It is possible that the ability of a metal carbonyl to undergo sonochemical reactions is influenced by its ability to enter the cavitation space. These reactions are possible in a wide range of solvents with the reaction rates being greatly influenced by the vapor pressure of the solvent. In addition the solvent may exhibit primary sonochemical reactions which can affect the metal complex in solution. Finally, reduction of CO to CH_4 and CH_3OH was observed at appreciable rates at low temperature and pressure in the absence of any metal species.

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