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Sonochemistry of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

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Abstract: Irradiation of liquids with high-intensity ultrasound creates, via cavitation, localized hot spots with transient pressures of >300 atm and temperatures ~3000 K. We report the first studies of the chemical effects of ultrasound on $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$. Ultrasonic irradiation of $Mn_2(CO)_{10}$ produces ligand substitution by phosphines or phosphites. The rate of this substitution is independent of the choice of ligand or of its concentration, and the mechanism of substitution does *not* involve metal–metal bond cleavages. $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ do not undergo sonochemical ligand substitution at appreciable rates, presumably because their lower vapor pressures preclude their presence in the cavitation event. In addition, we have found that $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ undergo rapid sonochemical halogenation with halocarbon solvents, with rate enhancement of 10^5. The primary sonochemial event in these halogenations is homolysis of the solvent, generating halogen atoms (which can be trapped by $M_2(CO)_{10}$ or by alkane solvent) and carbon radicals (which dimerize and have been so characterized).

The group 7B metal carbonyls provide an ideal system for the comparison of metal–ligand to metal–metal reactivity. The recent interest in their thermal[1] and photochemical[2] behavior has led us to initiate the investigation of the sonochemistry of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$. Sonochemistry originates from the creation of acoustic cavitation[3] by high-intensity ultrasound; this rapid formation, growth, and violent collapse of gas vacuoles in liquids generate short-lived (<nanosec) localized hot spots whose peak temperatures and pressures have been measured at ~3000 K and ~300 atm,[4] confirming earlier calculations.[5] Analogies to photochemistry, radiolysis, radio-frequency discharge, and other high-energy processes can be made. Several recent reports on the chemical effects of ultrasound in heterogeneous[6] and homogeneous[7] systems may be noted.

Both photochemical and thermal substitution of $M_2(CO)_{10}$ (M = Mn, Re) with phosphines or phosphites lead to predominantly axially disubstituted products,[1,2] with monosubstituted dinuclear species being observed[1a,b] under certain circumstances. Both metal–metal bond cleavage and CO ligand dissociation have been proposed as the initial step in these reactions. The photochemical reaction is believed to proceed through initial metal–metal bond cleavage,[2,8] followed by either dissociative or associative pathways, as shown in Scheme I.

Scheme I. Photochemical Pathways of $M_2(CO)_{10}$ Substitution

$$M_2(CO)_{10} \xrightarrow{h\nu} M(CO)_5 \tag{1}$$

$$M(CO)_5 \rightarrow M(CO)_4 + CO \tag{2}$$

$$M(CO)_4 + L \rightarrow M(CO)_4L \tag{3}$$

$$2M(CO)_4 \rightarrow M_2(CO)_8 \tag{4}$$

$$M(CO)_5 + L \rightarrow [M(CO)_5L]^{\ddagger} \rightarrow M(CO)_4L + CO \tag{5}$$

$$2M(CO)_4L \rightarrow M_2(CO)_8L_2 \tag{6}$$

$$M_2(CO)_8 + 2L \rightarrow M_2(CO)_8L_2 \tag{7}$$

The mechanism of the thermal reaction has been a matter of debate. The thermal substitution (at 140 °C) of $MnRe(CO)_{10}$ has been recently shown to involve principally initial loss of CO, with metal–metal bond cleavage as a minor pathway at best.[1a,b] In this case, $MnRe(CO)_9L$ is observed as the initial product[1a] that undergoes further substitution to yield $MnRe(CO)_8L_2$, as in Scheme II. Very recently, crossover labelling experiments have confirmed that CO dissociation is also the primary pathway for thermal substitution of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.[1e,f]

Scheme II. Thermal Pathways of $M_2(CO)_{10}$ Substitution

$$M_2(CO)_{10} \xrightarrow{\Delta} M_2(CO)_9 \tag{8}$$

$$M_2(CO)_9 + L \rightarrow M_2(CO)_9L \tag{9}$$

$$M_2(CO)_9L \xrightarrow{\Delta} M_2(CO)_8L \tag{10}$$

$$M_2(CO)_8L + L \rightarrow M_2(CO)_8L_2 \tag{11}$$

A second class of well-studied reactions of $M_2(CO)_{10}$ is halogenation to yield $M(CO)_5X$. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are halogenated[9] at room temperature with Cl_2 and Br_2 and at 40 °C with I_2. $Mn_2(CO)_{10}$ also undergoes a photochemical halogenation[2] with CCl_4 or $C_6H_5CH_2Cl$ to give $Mn(CO)_5Cl$. The proposed

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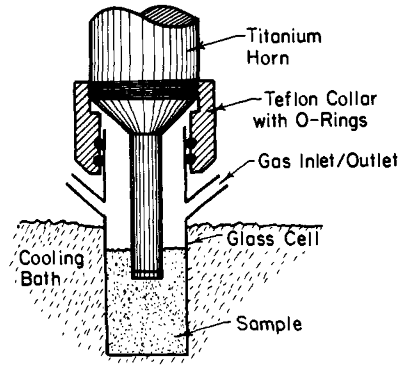

Figure 1. Inert atmosphere sonication reactor. Horn area is 1 cm^2; reaction vessel diameter as shown is 25 mn and will sonnicate 5–15 mL.

mechanism of the photochemical halogenation involves initial metal–metal bond cleavage and subsequent halogen atom abstraction:[2,8]

$$M_2(CO)_{10} \xrightarrow{h\nu} M(CO)_5\cdot \tag{12}$$

$$M(CO)_5\cdot + RX \rightarrow M(CO)_5X + R\cdot \tag{13}$$

$$2R\cdot \rightarrow R_2 \tag{14}$$

We report here the first studies of ultrasonically induced ligand substitution and halogenation of group 7B carbonyls. $Mn_2(CO)_{10}$, but not $MnRe(CO)_{10}$ or $Re_2(CO)_{10}$, will undergo sonochemical ligand substitution with phosphines or phosphites to produce $Mn(CO)_8L_2$. In addition, ultrasonic irradiation of $M_2(CO)_{10}$ in halocarbon solvents rapidly produces $M(CO)_5X$ with rate enhancements $>10^5$.

Experimental Section

All ultrasonic irradiations were made with a collimated 20-kHz beam from a lead zirconate titanate transducer with a titanium amplifying horn (Heat-Systems Ultrasonics, Inc., Model W375-P) directly immersed in the solution. Total acoustic power was ~100 W and acoustic intensities at the transducer surface were ~100 W/cm^2. The reactions were performed in a glass sonication cell under an Ar atmosphere, as illustrated in Figure 1. The sonication cell can be made in various volumes from 5 to >100 mL; temperature control, however, becomes more difficult at the smallest volumes. This can be critical since sonications must be made under conditions of low solvent volatility. If the vapor pressure of the solvent is large, effective compression of the cavities does not occur, and the local heating is lost.[7f,h] Thus, all sonications reported herein are performed at subambient temperatures near the freezing point of the solvent mixture.

Solvents were spectrophotometric or reagent grade and purified in the usual ways.[10] $Mn_2(CO)_{10}$ was obtained from Alfa-Ventron and vacuum sublimed before use. $Re_2(CO)_{10}$ was used as obtained from Strem Chemicals. $MnRe(CO)_{10}$ was prepared as described by Wrighton[2c] with a compact Xe arc lamp (Varian-Eimac). Triphenylphosphine was obtained from Aldrich and recrystallized from ethanol. Other phosphines and phosphites were used as supplied from Aldrich.

Infrared analysis utilized a Nicolet MX-5 Fourier transform infrared spectrophotometer. Quantitative analysis relied on the reported extinction coefficients of the complexes in question[11] and are accurate to ±15%. 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.

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.

Table I. Rates of Sonochemical Ligand Substitution of $M_2(CO)_{10}$

complex	ligand	rate,[a] μM/min
0.10 M $Mn_2(CO)_{10}$	0.20 M $P(C_6H_5)_3$	21
0.10 M $Mn_2(CO)_{10}$	0.10 M $P(C_6H_5)_3$	20
0.033 M $Mn_2(CO)_{10}$	0.10 M $P(C_6H_5)_3$	7.7
0.010 M $Mn_2(CO)_{10}$	0.10 M $P(C_6H_5)_3$	3.3
0.010 M $Mn_2(CO)_{10}$	0.033 M $P(C_6H_5)_3$	3.2
0.010 M $Mn_2(CO)_{10}$	0.020 M $P(C_6H_5)_3$	3.0
0.010 M $Mn_2(CO)_{10}$	0.010 M $P(C_6H_5)_3$	2.8
0.010 M $Mn_2(CO)_{10}$	0.020 M $P(OC_2H_5)_3$	3.0
0.010 M $Mn_2(CO)_{10}$	0.020 M $P(OC_6H_5)_3$	2.0
0.010 M $Mn_2(CO)_{10}$	neat $P(C_4H_9)_3$	1.5
0.05 M $Re_2(CO)_{10}$	0.1 M $P(C_6H_5)_3$	<0.05
0.02 M $MnRe(CO)_{10}$	0.04 M $P(C_6H_5)_3$	<0.05

[a] All reactions run in decane at −12 °C under Ar, except $P(C_4H_9)_3$ which was used as solvent at −5 °C. Error limits estimated as less than ±15%.

Table II. Rates of Sonochemical Reaction of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with Halogenated Solvents

complex	solvent	temp,[a] °C	rate,[b] μM/min
0.0025 M $Mn_2(CO)_{10}$	$CHBr_2CHBr_2$	16	2200
0.01 M $Mn_2(CO)_{10}$	CCl_4	−2	83
	$CHCl_3$	−45	55
	CH_2Cl_2	−52	2
	$CHBr_3$	23	5000
0.02 M $Mn_2(CO)_{10}$	$CHBr_3$	23	5000
0.04 M $Mn_2(CO)_{10}$	$CHBr_3$	23	5000
0.0025 M $Re_2(CO)_{10}$	$CHBr_2CHBr_2$	16	2000
0.01 M $Re_2(CO)_{10}$	CCl_4	−2	21
	$CHCl_3$	−45	30
	$CHCl_3$	−52	66
	CH_2Cl_2	−52	2
	$CHBr_3$	23	2000

[a] Thermocouple measurements during sonication within the reaction vessel. [b] Disappearance of $M_2(CO)_{10}$; the only observed product was $M(CO)_5X$; error limits ±2μM/min or 5%.

During ultrasonic irradiation, a modest initial temperature rise was observed by an iron–constantan thermocouple probe located in the center of the sonicated solution; a steady-state temperature was 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

Sonication of $Mn_2(CO)_{10}$ in alkane solutions of phosphines or phosphites leads to axially disubstituted $Mn_2(CO)_8L_2$. The rates of this substitution are roughly first order in $Mn_2(CO)_{10}$ concentration and independent of choice of ligand. Table I summarizes these experiments. In all cases only disubstituted species were observed.

Sonication of $Re_2(CO)_{10}$ with various concentrations of $P(C_6H_5)_3$ and $P(n\text{-}C_4H_9)$ produced no substitution even after sonication of up to 100 h. Sonication of 0.01 M $Re_2(CO)_{10}$ in neat $P(OC_2H_5)_3$ gave no substitution products after 20 h. In contrast, short photolysis with a Pyrex-filtered Xe arc produces complete disappearance of infrared bands due to $Re_2(CO)_{10}$ with the appearance of new bands at 1979 and 1947 cm^{-1} in decane. $MnRe(CO)_{10}$ also failed to yield any sonochemical ligand substitution in the presence of $P(C_6H_5)_3$ or any homometallic products in its absence, even after prolonged sonication. Similarly $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, when sonicated together in alkane solution, do not produce $MnRe(CO)_{10}$.

Very different reactivity is observed upon sonication in halocarbon solvents: the halogenated $Mn(CO)_5X$ is rapidly produced, as in eq[12] 15. As summarized in Table II, quantitative yields

$$M_2(CO)_{10} + 2R_3C\text{–}X \;\text{—)))}\!\rightarrow\; 2M(CO)_5X + R_3C\text{–}CR_3 \tag{15}$$

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of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br) are observed at appreciable rates in several halocarbons, producing complete conversions in minutes to hours. Control reaction mixtures in CCl_4, $CHCl_3$, and CH_2Cl_2 left in the dark and quiet at 25 °C showed no reaction after 24 h; in $CHBr_3$ at 40 °C, the control showed no reaction after 48 h. We estimate our detection limit to be <0.05 μM/min under these conditions. Therefore, ultrasonic irradiation has enhanced the rate of halogenation by as much as 10^5.

Alkane solutions of various halocarbons, even when quite concentrated (5 M), do not halogenate $M_2(CO)_{10}$ upon sonication. VPC analysis of alkane–halocarbon mixtures after sonication (including decane or heptane and $CHBr_2CHBr_2$ or CCl_4) shows significant yields of monohalogenated alkanes and HX at rates comparable to those shown in Table II. Finally, benzyl chloride, either neat or in alkane solution, does not sonochemically halogenate $M_2(CO)_{10}$ even after exhaustive sonication.

Discussion

Interesting comparisons can be made between the sonochemistry and the photo- and thermal chemistry of $M_2(CO)_{10}$. For example, does the very high peak temperatures of ultrasonic cavitation lead to carbonyl loss, as in moderate temperature pyrolysis, or to metal–metal bond cleavage, as in photolysis? The present experiments suggest the former. While ligand substitution can occur via either mechanism (Schemes I and II), if metal–metal bond cleavage occurs and $M(CO)_5\cdot$ is produced, halogen atom abstraction from benzyl chloride becomes a facile reaction.[2c] As noted earlier, sonication of $Mn_2(CO)_{10}$ in the presence of benzyl chloride does *not* yield $Mn(CO)_5X$, in keeping with the thermal mechanism of carbonyl loss. The kinetics of sonochemical ligand substitution are consistent with sonochemical CO dissociation: the rate of substitution is independent of both choice and concentration of phosphine or phosphite and is essentially first order in $[Mn_2(CO)_{10}]$.

More definitive in this argument would be the failure of sonication of $MnRe(CO)_{10}$ to produce $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, except that sonochemical ligand substitution of $MnRe(CO)_{10}$ also does not occur. Possible hypotheses for the sonochemical inertness of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ include the following: (1) cavitational heating is insufficient to induce metal–metal bond cleavage or CO dissociation; (2) recombination of the initial products (e.g., $M(CO)_5\cdot$ or $M_2(CO)_9$ with CO) within the cavitation event is more rapid than trapping with phosphine or phosphite; or (3) low volitivity precludes the presence of $Re_2(CO)_{10}$ or $MnRe(CO)_{10}$ from the cavitation vacuole, thus preserving them from the localized hot spot. The first hypothesis is very unlikely, since ultrasonic cavitation is capable of cleaving even C–C and C–H bonds,[3,7h] and there is not a great difference[12] in bond strengths or recombination rates[13] among $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$. The second hypothesis is also unlikely, since sonication of $MnRe(CO)_{10}$ does not yield $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ and since substitution does not occur even in neat $P(OC_2H_5)_3$. The third hypothesis is plausible and has been suggested before to explain the sonochemistry of arenes.[14] The heats of sublimation of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$ are reported[15] as 15.7, 16.4, and 18.5 kcal/mo, respectively. By extrapolating the published[15] vp–*T* relationships, we estimate the vapor pressures of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$ to be roughly 10^{-3}, 10^{-4}, and 10^{-5} torr, respectively, under the conditions used for sonication. One might expect that sonication of $MnRe(CO)_{10}$, for example, at higher temperatures, where its vapor pressure becomes comparable to $Mn_2(CO)_{10}$, would produce sonochemical ligand substitution. Unfortunately, thermal substitution begins to occur before the vapor pressure of $MnRe(CO)_{10}$ can become significant. Further work is under way to explore the effect of substrate volatility on sonochemical reactivity.

The sonochemical production of $M(CO)_5X$ in halocarbon solvents probably does not proceed through initial metal–metal bond cleavage as in the photochemical halogenation[2c] but is a secondary reaction of species produced directly from sonication of the solvent. Sonication of CCl_4 is known[16] to produce $Cl\cdot$, Cl_2, and organic radicals, which can then react with other species in solution by thermal pathways. For $CHCl_3$ we have observed that sonication under conditions used for halogenation of $M_2(CO)_{10}$ produces $CHCl_2CHCl_2$ at 133 μM/min in the absence of any metal complex. Thus, the sonochemical rate of $Cl\cdot$ and Cl_2 production is fast enough to generate the observed yields of $M(CO)_5Cl$. In addition, the lack of rate dependence on $Mn_2(CO)_{10}$ concentration confirms that the primary sonochemical reaction does not involve the metal carbonyl. We propose, then, the following eraction scheme:

$$R_3XC \text{ —)))}\rightarrow R_3C\cdot + X\cdot \qquad (16)$$

$$2R_3C\cdot \rightarrow R_3CCR_3 \qquad (17)$$

$$2X\cdot \rightarrow X_2 \qquad (18)$$

$$M_2(CO)_{10} + 2X\cdot \rightarrow 2M(CO)_5X \qquad (19)$$

$$M_2(CO)_{10} + X_2 \rightarrow 2M(CO)_5X \qquad (20)$$

In keeping with this mechanism, alkane solutions of halocarbons do not halogenate $M_2(CO)_{10}$, due to trapping of $X\cdot$ by the alkane via well-known radical abstraction pathways.[17] Confirmation has been made by the observation of halogenated alkane products and HX, as discussed earlier.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $MnRe(CO)_{10}$, 14693-30-2; $Re_2(CO)_{10}$, 14285-68-8; $P(C_6H_5)_3$, 603-35-0; $P(OC_2H_5)_3$, 122-52-1; $P(OC_6H_5)_3$, 101-02-0; $P(C_4H_9)_3$, 998-40-3; $CHBr_2CHBr_2$, 79-27-6; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; $CHBr_3$, 75-25-2.

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