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High-Pressure Reactions of Small Covalent Molecules. 11. Synthesis of Transition-Metal Carbonyls from Metal Oxides[1]

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The synthesis of transition-metal carbonyls from carbon monoxide and an appropriate oxide is thermodynamically possible for all of the transition metals at 25 °C (1 atm) according to the equation

$$MO_x + (x + y)CO \rightarrow M(CO)_y + xCO_2$$

This synthetic procedure, however, has been reported only for $Os(CO)_5$,[3] $Tc_2(CO)_{10}$,[4] $Re_2(CO)_{10}$,[5] and a rhodium carbonyl.[6] The direct reaction using carbon monoxide as the reducing agent is very convenient since hydrogen–carbon monoxide mixtures are not required and no other reagents are used which could contaminate the product; however, this reaction has not been reported for the synthesis of metal carbonyls which are commercially available. This study was undertaken to provide samples of isotopically pure metal carbonyls for spectroscopic studies[7] and then was expanded to include a study of the parameters required for the synthesis of $Mo(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$, and $Fe(CO)_5$ from an oxide.

Results and Discussion

The experimental results summarized in Table I describe the reaction conditions for an observable reaction and outline as well the conditions suitable for the synthesis of the transition-metal carbonyls. Additional experiments were carried out to determine if increased pressure changed the equilibrium constant or the rate of the reaction. In all cases when the experiments were permitted to extend for several days, the yields were nearly quantitative which indicated the function of pressure is to increase the rate of reaction.

The reaction of carbon monoxide with MoO_3 and WO_3 results in a nearly quantitative yield of the corresponding hexacarbonyl at 300 °C (2000 atm) within 12 h. However, lower yield reactions do take place at lower temperatures and pressures. The formation of these substances near 200 °C with 100–500 atm of carbon monoxide corresponds to conditions which have been reported for their synthesis from the metal.[8,9] However, in this laboratory the carbonyls would not form from metal powders at these or more rigorous conditions. When CrO_3 or Cr_2O_3 was combined with carbon monoxide at similar conditions, no $Cr(CO)_6$ was obtained; however, CrO_3 was converted to Cr_2O_3.

The reaction of cobalt(II) oxide with carbon monoxide results in a quantitative yield at 80 °C (1900 atm), but no reaction takes place at 50 °C (2450 atm) and only a low yield is obtained at 128 °C (340 atm). No $Co_4(CO)_{12}$ was obtained in any of the experiments even when the synthesis was carried out at temperatures up to 300 °C. The low temperature observed for excellent yields parallels the relatively low-temperature (150 °C) reaction of carbon monoxide (40 atm) with cobalt metal which had been formed by the hydrogen reduction of cobalt(II) oxalate.[10,11]

The synthesis of $Fe(CO)_5$ also takes place at relatively mild conditions with an 80% yield being obtained at 225 °C (2000 atm). The ease of this reaction was anticipated because of the mild conditions required for its synthesis from the metal. The carbon monoxide used in this study contained traces of $Fe(CO)_5$ which presumably formed from the steel storage cylinder; however, experiments with isotopically pure iron(II) oxide indicated that the amount of initial $Fe(CO)_5$ was insignificant compared to the observed reaction yields.

Table I. Transition-Metal Oxide Reactions with Carbon Monoxide[a]

P, atm	*T*, °C	Convrsn, %	*P*, atm	T, °C	Convrsn, %
Molybdenum(VI) Oxide					
550	185	5	3640	140	0
1300	195	5	2175	160	0
750	240	5	540	185	0
130	285	5	100	210	0
2000	300	89	400	235	0
750	350	11	275	360	0
1350	400	81			
Tungsten(VI) Oxide					
3500	265	85	3300	190	0
475	265	5	2600	205	0
2000	300	85	2300	230	0
375	355	5	550	260	0
Cobalt(II) Oxide					
2000	80	100	2000	25	0
340	128	10	2450	50	0
1850	128	100			
Iron(III) Oxide					
3300	175	30	2400	150	0
1250	225	50	1900	175	0
2000	225	80	1360	200	0
			680	225	0

[a] Conversion based on the quantity of metal oxide employed. All reactions were for 24 h.

The disproportionation of carbon monoxide was also observed in this study. This reaction cannot be correlated with the conditions required for the formation of a metal carbonyl, but the conditions required for disproportionation are a function of the employed metal oxide. The oxides of cobalt (e.g., 150 °C and 100 atm) and iron (e.g., 150 °C and 600 atm) required the least rigorous conditions while the chromium (e.g., 500 °C and 2000 atm) and tungsten (e.g., 450 °C and 600 atm) oxides required the most rigorous conditions for disproportionation. Molybdenum(VI) oxide has an easily defined region of minimum conditions from 140 °C (3500 atm) to 225 °C (600 atm) where disproportionation occurs. Experimentally this reaction was not desirable because at times the microreactor would become filled with finely divided carbon.

Experimental Section

A borosilicate glass vacuum system with Teflon stopcocks (Fischer & Porter Co., Warminster, Pa.) was employed to purify and analyze volatile materials. High pressures were generated using a carbon monoxide gas pressure booster (High Pressure Equipment Co., Erie, Pa.) attached to a high-pressure, high-temperature hydrothermal research unit (Model HR-1B-4, Tem-Pres Research, State College, Pa.,).[12,13] The transition-metal oxides were placed in 5-mm glass liners which were placed into the high-pressure microreactors (Model MR-114-R, Tem-Pres Research). At the end of a reaction period, the reactor was vented and then opened. Volatile transition-metal carbonyls were collected directly in the vacuum line and nonvolatile materials were mechanically recovered (using a glovebag under an argon atmosphere if necessary). All products were identified and confirmed by two or more techniques including infrared spectroscopy, mass spectroscopy, elemental analysis, and gas-phase molecular weight measurement.

Good yields of metal carbonyl can also be obtained when the pressure is generated by condensing carbon monoxide into a microreactor at −196 °C for 1 h. This procedure generates 700 atm at room temperature and 1000 atm at 350 °C.

Instrumentation. Infrared absorption spectra were obtained in the 4000–300-cm^{-1} region using a Beckman Model IR-10 double-beam, grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. Nonvolatile materials were examined as mineral

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oil mulls. The instrument was calibrated using polystyrene. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Reagents. The transition-metal oxides were commercially available and Linde commercial grade (98.0%) carbon monoxide was used.

Representative Reactions

Additional experiments are summarized in Table I. In all cases 1–2 mmol of metal oxide was used.

Reaction of Fe_2O_3. Commercial Fe_2O_3 (160 mg, 1.00 mmol) was placed into a borosilicate glass tube (5 mm × 100 mm) which was then packed with borosilicate glass wool. The liner was then inserted into the microreactor which was sealed, pressured to 2000 atm with carbon monoxide, and heated at 300 °C for 24 h. At the end of the reaction period, the bomb was cooled to room temperature, attached to a vacuum line, and carefully opened into a series of two traps cooled to −196 °C. The material which stopped in these traps was combined into one trap and then passed through a trap cooled to −96 °C (toluene slush) into a trap cooled to −196 °C. The −196 °C trap contained carbon dioxide and the −96 °C trap contained $Fe(CO)_5$ (376 mg, 1.92 mmol).

Reaction of MoO_3. Commercial MoO_3 (158 mg, 1.10 mmol) was placed into a glass tube (5 mm × 10 mm) which was then packed with borosilicate glass wool. The liner was then inserted into the microreactor which was sealed, pressured to 2000 atm, and heated at 300 °C for 24 h. At the end of the reaction period, the reactor was cooled to room temperature and then vented into a fume hood. The molybdenum hexacarbonyl (261 mg, 0.989 mmol) was recovered by removing the glass liner, crushing it, and then subliming the product at 40 °C (0.01 Torr).

Additional Reactions. The above procedure was used to prepare $W(CO)_6$ and $Co_2(CO)_8$ except the latter substance was handled in an argon-filled glovebag.

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Registry No. $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_5$, 13463-40-6; CO, 630-08-0; Fe_2O_3, 1309-37-1; MoO_3, 1313-27-5; WO_3, 1314-35-8; CoO, 1307-96-6.

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Photochemical Primary Processes in Copper(I) Complexes. A Probe for Charge Transfer to Solvent and Charge Transfer to Ligand Excited States

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Photochemical studies of Cu(I) complexes have shown that the reducing tendencies of these systems are enhanced when irradiated with ultraviolet or visible light. A photoinduced reduction of Co(III) complexes by bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu(dmp)_2{}^+$, was reported by McMillin et al.[1] The reduction of Co(III) complexes associated with Cu(I) has been examined by Hurst and co-workers by irradiations of the ligand field bands of the cobalt fragment. They attributed this reaction to an intramolecular electron-transfer process from Cu(I) to Co(III).[2] Also Stevenson and Davis[3] found that evolution of hydrogen and oxidation to cupric ions, as indicated in eq 1, takes place by irradiation of acidic

$$CuX_3{}^{2-} \xrightarrow[+H^+]{h\nu} CuX_3{}^- + {}^1/_2H_2 \qquad (1)$$

$$X^- = Cl^- \text{ or } Br^-$$

solutions of copper(I) halides. Although the role of the intermediates might be very important for any explanation of the photochemical properties of these systems, no efforts have been made to establish their nature. Evidence is provided here for the formation of solvated electrons in the primary process of cuprous halides[4] with subsequent generation of a transient hydride complex. By contrast, the main features of the primary process of $Cu(dmp)_2{}^+$[5] are correlated with radical formation.

Experimental Section

Continuous way irradiations were performed using a 4000 Rayonet photochemical reactor or a 300-W Eimac lamp coupled with a high-intensity Bausch and Lomb monochromator. Ferrioxalate was used as a primary actinometric reference.[6] The light intensity was checked frequently with $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5Br^{2+}$.

Conventional flash photolysis experiments were carried out in an apparatus built in this laboratory. The experimental setup will be described elsewhere.[8] Two flash lamps, FP-8-100 C purchased from Xenon Corp., were fired at energies between 40 and 400 J/flash producing pulses of light with a length of ~30 μs. Tests of the sensitivity, time resolution, and linear responses with flash energy were carried out with $Co(NH_3)_5Br^{2+}$ by already reported procedures.[9]

The preparation of the solutions for photolysis was accomplished as follows. Solid samples of the copper(I) compounds were dissolved in previously deaerated solutions containing the substrates required for the experiment. Solvents were deoxygenated with streams of nitrogen or nitrous oxide in a gastight apparatus. The ionic strength of the reaction medium was adjusted to 1.0 M with $HClO_4$, NaCl, and HCl as indicated elsewhere in the text.

Concentrations of cuprous chloride transformed into cupric species were estimated from spectral changes measured at 280 nm in a cell with 1 mm of optical path. Cu(II) was determined with I^-. Samples of irradiated solutions (1 cm^3) were mixed with 5 cm^3 of 0.2 M I^- and the final volume was adjusted to 10 cm^3 with distilled water. The optical density of $I_3{}^-$ was measured at 400 nm against blanks. Calibration curves were obtained for various concentrations of Cu(II) ($[Cu(II)] \leq 10^{-4}$ M) in the presence of Cu(I) ($[Cu(I)] \leq 10^{-2}$ M).

Yields of H_2 and N_2 are determined by gas chromatography. Hydrogen was also measured by mass spectroscopy. The solutions of cuprous complexes used in these experiments were degassed by three freeze–thaw cycles and saturated with He or N_2O at 1 atm. Gas products, noncondensables at −180 °C, were removed under vacuum from the reaction mixture.

Cuprous chloride, Baker Analyzed, was recrystallized three times from deaerated hydrochloric acid. Solid batches of the compound were manipulated under a nitrogen atmosphere and dried under vacuum. Cuprous bromide, also Baker Analyzed, was purified by a similar method. $[Cu(dmp)_2]ClO_4$ was synthesized and purified by reported procedures.[5] Other chemicals were reagent grade and used without further purification.

Results and Discussion

Photolyses at 280 nm of acid solutions ($[NaCl] + [HCl] = 1.0$ M; $1.0 \geq [HCl] \geq 0.1$ M) containing cuprous chloride ($C \leq 0.01$ M) produced hydrogen and cupric ions ($2\phi_{H_2} = \phi_{Cu^{2+}} = 0.33 \pm 0.04$) in agreement with the stoichiometry reported by Stevenson et al. (eq 1). However, *nitrogen was also found* as a reaction product in solutions saturated with N_2O. The yield of nitrogen increased with decreasing con-