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Homogeneous Catalysis of the Water Gas Shift Reaction with the Use of Group 6 Transition Metal Carbonyls:[1] $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

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Abstract: Measurements have been carried out to determine the rate of hydrogen production by the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) operating at temperatures of 200 °C and lower with hexacarbonyls of chromium, molybdenum, and tungsten serving as catalyst precursors in basic methanol–water solutions. The catalytic behavior of each of these systems is similar and turnover numbers as great as 12000 mol of H_2/mol of metal hexacarbonyl per day can be achieved at 200 °C. The rate of hydrogen production is found to be (a) proportional to the amount of metal hexacarbonyl present in the system, (b) inversely proportional to carbon monoxide pressure; and (c) increasing with base concentration. Under conditions of constant base concentration and pressure, the temperature dependence of this reaction is found to be quite similar for each system corresponding to activation energies of 35, 35, and 32 kcal/mol for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively. The overall kinetics of this reaction can be explained by a mechanism involving formate decomposition rather than activation of carbon monoxide.

The water gas shift reaction finds extensive use in industry as a means for enriching the hydrogen content of water gas (synthesis gas). Current technology involves reacting steam with the carbon monoxide of the synthesis gas in two stages over iron oxide–chromium oxide and zinc oxide–copper oxide catalyst beds, respectively, with the temperature of the former being in excess of 300 °C.[2] The reaction and associated thermodynamic parameters are:

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad (1)$$

$$\Delta G^\circ_{298} = -6.82 \text{ kcal};\ \Delta H^\circ_{298} = -9.84 \text{ kcal};\ \Delta S^\circ_{298} = -10.1 \text{ cal/deg}$$

Recent investigations[3] have shown that this same reaction can be carried out at considerably lower temperatures ($T < 200$ °C) with water present as a liquid by using homogeneous catalysts to accelerate the reaction. The equation and thermodynamic parameters associated with this latter reaction are:

$$CO(g) + H_2O(l) \rightleftharpoons H_2(g) + CO_2(g) \qquad (2)$$

$$\Delta G^\circ_{298} = -4.76 \text{ kcal};\ \Delta H^\circ_{298} = +0.68 \text{ kcal};\ \Delta S^\circ_{298} = +18.3 \text{ cal/deg}$$

It is seen from eq 2 that with water present in a condensed state, the water gas shift reaction is mildly endothermic yet highly favored from the standpoint of free energy because of the large positive entropy change associated with this latter reaction.

The interest in carrying out the water gas shift reaction with the use of liquid water (reaction 2) rather than steam (reaction 1) stems from two considerations. First, as mentioned above, the lower operating temperature and use of liquid water rather than steam offer the possibility of considerable savings in energy in comparison to conventional processes which utilize reaction 1. Second, the fact that the reaction is mildly endothermic offers an advantage from an engineering standpoint in that any isothermal shift reactor designed around this latter reaction (reaction 2) will have greatly reduced cooling demands in comparison with currently used reactors.

This paper is the second in a series intended to assess the operational characteristics and kinetics of homogeneous catalyst systems capable of catalyzing reaction 2 under relatively mild conditions. The first paper of this series concerned iron pentacarbonyl, $Fe(CO)_5$.[3p] It was shown that with $Fe(CO)_5$ serving as a catalyst in basic alcohol–water solutions, the water gas shift (wgs) reaction was zero order with respect to carbon monoxide and had a temperature dependence corresponding to an activation energy of 22 kcal/mol. The base used in these experiments was KOH. However, it was shown in this previous work that the KOH reacted rapidly with CO in the initial stages of each reaction to produce potassium formate quantitatively. As a result $KHCO_2$ was the base present over essentially the entire course of each reaction. With $Fe(CO)_5$ the rate of production of hydrogen was found to be effectively independent of the concentration of KOH, hence $KHCO_2$, in the reaction mixture. The results of the experiments described in this paper show that reaction 2 exhibits markedly different kinetics when catalyzed by the hexacarbonyls of the group 6B transition metals $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ under similar conditions.

Experimental Section

The experimental apparatus and procedures used in this work are the same as those employed in earlier studies with $Fe(CO)_5$. A detailed description of these can be found in ref 3p. Consequently only a brief overview of the apparatus and experimental methods employed in this work will be given here for the sake of clarity.

The water gas shift reactions were carried out in small unlined stainless steel (type 304) autoclaves having an internal volume of 700 mL. Each autoclave was mounted in an electrical oven and the temperature of the contents was regulated with a proportional controller by using a thermocouple sensor mounted in a thermocouple well extending into the interior of the autoclave. After an initial warm-up period (~25 min) temperatures within a given autoclave could be maintained constant to within ±1 °C with this control system. The pressure of the contents was monitored throughout each experiment by using a Bourdon gauge

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[2] Thomas, C. L. "Catalytic Processes and Proven Catalysts"; Academic Press: New York, 1970.

[3] (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252. (b) Pettit, R.; Mauldin, C.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 151. (c) Kang, H.; Mauldin, C.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323. (d) Cheng, C. H.; Hendriksen, D. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 2791. (e) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D. *Ibid.* **1978**, *100*, 3942. (f) Yoshida, T.; Ueda, Y.; Otsuka, S. *Ibid.* **1978**, *100*, 3942. (g) Cheng, C. H.; Eisenberg, R. *Ibid.* **1978**, *100*, 5968. (h) Laine, R. M. *Ibid.* **1978**, *100*, 6451. (i) Laine, R. M.; Thomas, D. W.; Carry, L. W.; Buttrill, S. E. *Ibid.* **1978**, *100*, 6527. (j) Ford, P. C.; Rinker, R. G.; Laine, R. M.; Ungerman, C.; Landis, V.; Moya, S. A. *Adv Chem. Ser.* **1979**, *173*, 81. (k) Frazier, C. C.; Hanes, R.; King, A. D.; King, R. B. *Ibid.*, p 9. (l) Pettit, R.; Cann, K.; Cole, T.; Mauldin, C. H.; Slegeir, W. *Ibid.*, p 121. (m) Ford, P. C.; Rinker, R. G.; Ungerman, C.; Laine, R. M.; Landis, V.; Moya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595. (n) Ungerman, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *Ibid.* **1979**, *101*, 5922. (o) Baker, E. C.; Hendriksen, D. E.; Eisenberg, R. *Ibid.* **1980**, *102*, 1020. (p) King, A. D.; King, R. B.; Yang, D. B. *Ibid.* **1980**, *102*, 1028. (q) King, A. D.; King, R. B.; Yang, D. B. *Chem.Commun.* **1980**, 529.

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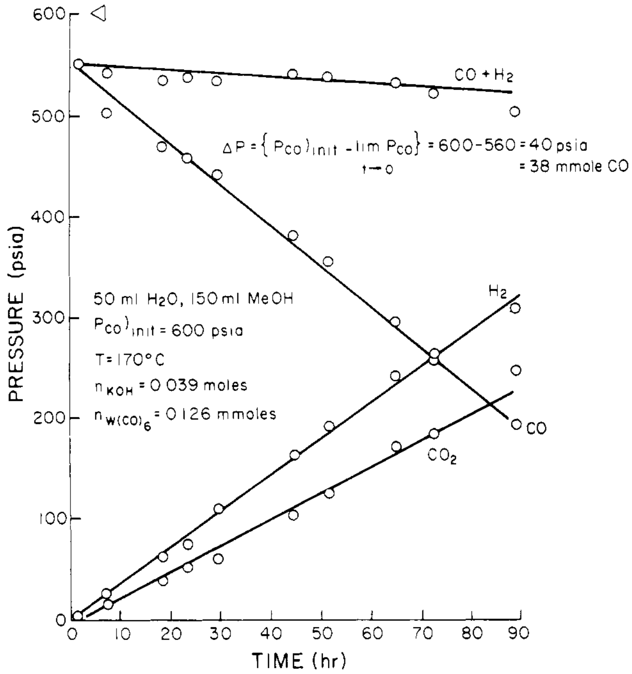

Figure 1. Partial pressures of H_2, CO_2, and CO as a function of time. Catalyst solution: $W(CO)_6$ (0.126 mmol), KOH (39 mmol), 25% H_2O–75% CH_3OH (200 mL). Temperature: 170 °C. Loading pressure of CO corrected to 170 °C: 600 psia.

mounted through the closure at the top of each autoclave. Magnetic stirring was used for agitation. Glass liners were available for the small autoclaves used in these experiments. However, preliminary experiments showed that the rates of hydrogen production were the same in the presence or absence of these liners. Therefore, liners were not used in order to facilitate these experiments.

The composition of the gas mixture (CO, CO_2, Ar, H_2) above the solution within the autoclave was analyzed with a Fisher Model 1200 gas partitioner, using helium as the carrier gas. Care was taken to ensure that all hydrogen analyses were performed within the linear response region of the sensitivity curve for this gas. Argon was used as an internal standard. Gas sampling was accomplished by using gas syringes and a simple loading system described previously.[3p] Two methods were used to compute gas compositions expressed as partial pressures. Both required the prior determination of external sensitivity factors for each gas. The first method required that the pressure of the contents in the bomb be recorded at the time each gas sample was taken. The pressure reading was corrected to the total pressure of noncondensable gases by subtracting solvent vapor pressure which had been determined previously. The individual partial pressures of the gases of interest were calculated by using this corrected total pressure and gas mole fractions obtained from the gas analysis according to Dalton's law. The second method used argon as an internal standard. Here the initial loading of CO and Ar was analyzed at room temperature prior to heating for a given experiment. The partial pressure of argon computed at room temperature was corrected to the elevated temperature of the experiment subsequently performed thus allowing partial pressures of the gases of interest to be computed directly by using argon as an internal standard. The relative merits of these two methods are discussed in an earlier paper.[3p] In every instance, partial pressures calculated according to these two methods were found to be in excellent agreement. The average error in H_2 partial pressure, derived from repetitive measurements, is ±3 psia while that for the other gases is ±1 psia.

All gases used were CP grade or the equivalent having quoted purities of 99.5% or better. Fisher certified ACS grade methanol and laboratory distilled water were used to make up the various solvent mixtures employed in these studies. Fisher certified ACS grade potassium hydroxide and practical grade potassium formate were employed as bases. The $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ used in these studies were obtained from Pressure Chemical Co. and were purified by vacuum sublimation before use.

Results and Discussion

A representative sample of the data obtained in these experiments is shown in Figure 1 where the partial pressures of CO, H_2, and CO_2 are shown plotted as a function of time over a 90-h period for an experiment conducted at 170 °C, using $W(CO)_6$ as a catalyst. In this particular experiment the autoclave was charged with 200 mL of a 25% water–75% methanol (v/v) solution containing 39 mmol of KOH and 0.125 mmol of $W(CO)_6$ pressurized under a mixture of CO and Ar with the partial pressure of CO being 406 psia prior to heating (T = 27 °C). This loading pressure of CO when corrected to 170 °C is 600 psia as indicated by the arrow along the vertical axis. Since a liquid loading of 200 mL is used here, the volume of gas in the autoclave is 700–200 = 500 mL. Thus, at 170 °C an increment in partial pressure of 1 psia corresponds to the production of (1/14.7)(0.50)/(0.082)(443) = 0.94 mmol of gas and vice versa. Thus, in the experiment shown in Figure 1, 200 psia of H_2 are produced in 55 h, corresponding to a rate of production of 200/55 = 3.63 psi h^{-1} = 3.42 mmol h^{-1}. Expressed in terms of turnover numbers, this rate is (3.42 mmol of H_2 h^{-1}/0.126 mmol of $W(CO)_6$) × 24 h day^{-1} = 650 day^{-1}.

The data shown in Figure 1 illustrate a number of features about the water gas shift (wgs) reaction operating with catalyst systems studied here. To begin with, the reaction is clearly catalytic with respect to both $W(CO)_6$ and base since beyond 10 h into the run the mmoles of H_2 produced exceeds the amounts of $W(CO)_6$ (0.126 mmol) and base (39 mmol) present in the system. Second, the fact that the sum of the partial pressures of CO and H_2 (indicated at the top of Figure 1) is nearly horizontal indicates that the mole consumption of CO exactly matches the production of H_2 as required by the stoichiometry of eq 1. Thus one infers that no side reactions occur over the course of the wgs reaction. However, at time zero this sum of partial pressures and the partial pressure of CO do not meet at 600 psia but rather intersect the vertical axis at a partial pressure of 560 psia. It follows therefore that the partial pressure of carbon monoxide present during the initial stages of the water gas shift reaction is P_{CO}^{init} = 560 psia rather than the expected value of 600 psia. The discrepancy between the loading pressure and P_{CO}^{init} is 40 psia or 38 mmol of CO, indicating that OH^- ion has reacted quantitatively with CO to produce formate ion prior to the onset of the wgs reaction. Varying amounts of KOH have been used in a series of similar experiments at various CO loading pressures and temperatures. In every case a quantitative conversion of OH^- to HCO_2^- is found to occur rapidly during the warm-up period prior to the onset of the wgs reaction. The reaction producing formate is found to be insensitive to both temperature and loading pressure of CO. Since carbon monoxide is always present far in excess of the amount of OH^-, this indicates that KOH acts as a limiting reagent in producing the weaker base potassium formate which in turn is the basic species present as the wgs reaction proceeds. Identical behavior is exhibited by these systems when triethylamine is used indicating that the corresponding ammonium formate is the base present during the wgs reaction. As expected, when sodium formate is used as the initial base in the methanol–water solution, the wgs reaction proceeds as usual but without any initial uptake of CO to produce formate ion, i.e., P_{CO}^{init} exactly equals the loading pressure of CO corrected to the temperature of the reaction.[4]

Finally, it is seen that the vapor concentration of CO_2 is considerably less than that of H_2 at all pressures in apparent violation of the stoichiometry demanded by eq 2. This cannot be attributed simply to the reaction of CO_2 with base to form bicarbonate in view of the fact that beyond 15 h into the reaction this discrepancy exceeds the total amount of base present in the reaction. In an earlier study involving $Fe(CO)_5$,[3p] a similar discrepancy was noted and it was shown that the difference in partial pressure of hydrogen, P_{H_2}, and carbon dioxide, P_{CO_2}, could be explained quan-

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(4) Similar observations have been made in an earlier study of this same reaction catalyzed by $Fe(CO)_5$.[3p] Also, as was found in this earlier work, samples removed from the liquid phase during the course of the water gas shift reaction have pH readings ranging from 8.6 in the early stages of the reaction to approximately 7.5 in the later stages of the reaction at high partial pressures of CO_2. As a comparison, solutions of 0.2 M sodium formate in the same alcohol–water mixture give pH readings of 8.6, thus serving to confirm the argument that the actual base present at the onset of the water gas shift reaction is formate ion regardless of the nature of the base added to the initial solution in these three cases.

Table I. The Effect of Solvent on the Rate of Production of H_2[a]

composition	rate, day^{-1} Cr(CO)$_6$ (180 °C)	Mo(CO)$_6$ (160 °C)	W(CO)$_6$ (160 °C)
10% H_2O-90% CH_3OH	2500	265	330
25% H_2O-75% CH_3OH	1570	220	270
50% H_2O-50% CH_3OH	480	40	115

[a] Solution: 200 mL of methanol-water mixtures of varying composition, each containing 39 mmol of KOH and 0.126 mmol of transition metal carbonyl. Loading pressure of CO: 400 psig at ~25 °C.

titatively in terms of differing solubilities of CO_2 and H_2 in the alcohol-water mixture accordinging to an equation

$$\frac{P_{CO_2}/P_{H_2}}{1 - P_{CO_2}/P_{H_2}} = (RTK_H(CO_2))^{-1}\left(\frac{V_g}{V_l}\right) \tag{3}$$

Here $K_H(CO_2)$ denotes the molar solubility of CO_2 in the liquid phase at 1 atm while R and T represent the universal gas constant and temperature, respectively. V_g and V_l represent the gas-phase and liquid-phase volumes within the autoclave. It is assumed in deriving eq 2 that the solubility of CO_2 far exceeds that of H_2 so that the solubility of H_2 can be considered negligible in comparison with that for CO_2. This equation predicts that the ratio of CO_2 and H_2 produced by the wgs reaction, P_{CO_2}/P_{H_2}, is independent of the total pressure and is solely a function of the CO_2 solubility and respective phase volumes. The solubility of CO_2 at 170 °C in a methanol-water mixture of the composition used here is unknown to these authors. However, a reasonable estimate can be made assuming that the solubility will be similar to that for CO_2 in pure methanol at this temperature: $K_H = 1.55 \times 10^{-2}$ mol L^{-1}/atm.[5] Thus, combining this with values of $V_g = 500$ mL and $V_l = 200$ mL, eq 3 predicts $P_{CO_2}/P_{H_2} = 0.8$ which is in surprisingly good agreement with the ratio $P_{CO_2}/P_{H_2} = 0.7$ exhibited by the data of Figure 1. Thus it is reasonable to attribute the bulk of difference in gas phase concentrations of H_2 and CO_2 seen in Figure 1 to carbon dioxide dissolved at relatively high concentrations in the condensed solvent phase within the autoclave.

The operational characteristics of the wgs reaction catalyzed by $Mo(CO)_6$ and $Cr(CO)_6$ are identical with those described above for $W(CO)_6$. Thus it can be concluded that for each system the wgs reaction proceeds with no competing side reactions and is catalytic with respect to base and transition metal carbonyl under the conditions of these experiments. Also, in addition to catalyst and the reactant water, the alcohol rich condensed phase contains formate ion at concentrations determined by the initial loading of base and dissolved CO.

In the presence of excess water, the wgs reaction can be expected to depend upon the following variables: (a) nature of the solvent, (b) concentration of the catalyst, (c) concentration of base, (d) carbon monoxide pressure, and (e) temperature.

Table I lists the rates of hydrogen production for a series of reactions which for a given metal carbonyl differ only with respect to the composition of the methanol-water mixture. It is seen that the less polar solvent mixtures containing 10% and 25% water by volume are superior to that containing 50% water in the reaction medium. The solubilities of these transition metal carbonyls in water are too low to allow a comparison to be made between these alcohol solutions and pure water.

The solubilities of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are very low in methanol-water mixtures at room temperature. Consequently it was not possible to examine the relationship between reaction rate and metal carbonyl concentration over a wide range of concentrations. However, rates of hydrogen production were compared for solutions (200 mL of 25% H_2O-75% methanol, 39 mmol of KOH) operating under identical conditions (160 °C, CO loading pressure of 400 psia) containing 0.063 and 0.126 mmol of $W(CO)_6$ and $Mo(CO)_6$ and the same amounts of $Cr(CO)_6$ at 180 °C. Within experimental error, the rates of hydrogen production were found to double as the concentration of each metal hexacarbonyl doubled; i.e., the rates of reaction expressed as turnover number (mol of H_2/mol of metal hexacarbonyl per day) were constant to within 10%. Thus the water gas shift reaction can be considered to be first order with respect to each of the transition metal hexacarbonyls under the experimental conditions employed here. In view of this, it is appropriate to tabulate all rate data as turnover numbers (mol of H_2/mol of $M(CO)_6$ per day)(M = Cr, Mo, W).

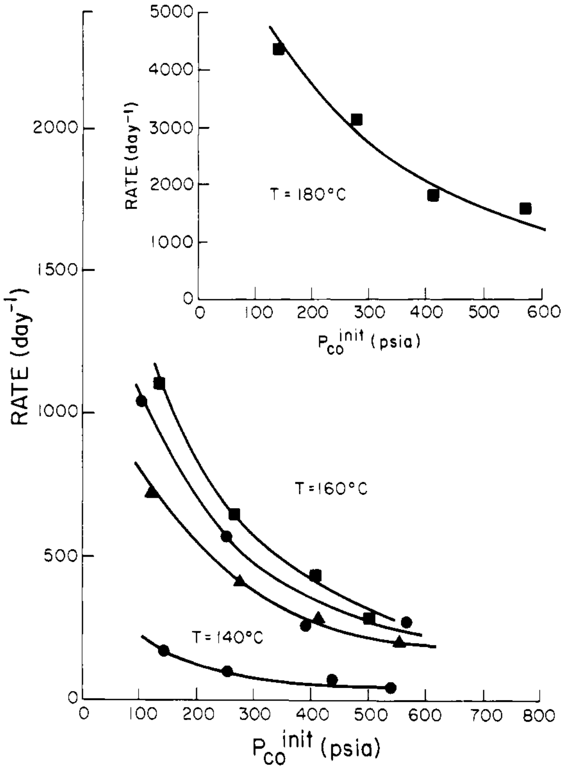

Figure 2. Rate of H_2 production measured at constant base concentration, [KOH] = 0.20 M, as a function of initial CO pressure. Catalyst solution: $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ (0.126 mmol), KOH (39 mmol), 25% H_2O-75% CH_3OH (200 mL). ■, $Cr(CO)_6$; ▲, $Mo(CO)_6$; ●, $W(CO)_6$.

Table II lists the rates of hydrogen production measured at a series of base concentrations and carbon monoxide pressures for each of the metal hexacarbonyls.

Rate data from Table II measured at constant base concentration, [KOH] = 0.20 M, are shown plotted as a function of P_{CO}^{init} for each metal carbonyl in Figure 2. It is seen that CO inhibits the wgs reaction and does so to about the same extent with each catalyst system. The rate data obtained with $W(CO)_6$ at constant base concentration ([KOH] = 0.20 M) and varying pressures is shown plotted as a function of $(1/P_{CO})_{init}$ in Figure 3; (data for T = 150, 180, and 200 °C are taken from Table III). It is seen that at all temperatures, the rate of hydrogen production is inversely proportional to the CO pressure. The data for $Cr(CO)_6$ and $Mo(CO)_6$ exhibit the same inverse dependence on CO pressure.

In Figure 4 the rate data measured for $W(CO)_6$ at a constant loading pressure of 400 psig are shown plotted as a function of base concentration for KOH, $NaHCO_2$, and $N(C_2H_5)_3$. The rate of H_2 production is seen to increase with base concentration irrespective of the specific nature of the base. The fact that the

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(5) The solubility of CO_2 in pure methanol has been determined at temperatures ranging from 0 to 75 °C by: (a) Krichevskii, I. P.; Lebedeva, E. S. *Zh. Fiz. Khim.* **1947**, *21*, 715. (b) Ohgaki, K.; Katayama, *T. J. Chem. Eng. Data* **1976**, *21*, 53. These data are found to vary linearly with T^{-1} indicating that the heat of solution is relatively insensitive to temperature. A linear extrapolation yields a mole fraction solubility of $X_{CO_2} = 7.7 \times 10^{-4}$ at 170 °C. A long extrapolation of the density function for methanol found in Washburn's work [Washburn, E. D., Ed. "International Critical Tables", McGraw-Hill: New York, 1928; Vol. 3, p 27] yields a value of $\bar{V} = 50$ cm^3/mol for the molar volume of methanol at 170 °C. This can be combined with the mole fraction solubility of CO_2 to yield a value of $K_H = X_{CO_2}/\bar{V} = 1.55 \times 10^{-2}$ M atm^{-1}.

Table II. The Effect of Base Concentration and Carbon Monoxide Pressure on the Rate of Production of H_2[b]

catalyst	temp, °C	base	[base], M	CO loading[a] pressure, psig	P_{CO}^{init}, psia	rate, day^{-1}
$Cr(CO)_6$	160	KOH	0.20	100	117	1100
	160	KOH	0.20	200	261	650
	160	KOH	0.20	300	405	530
	160	KOH	0.20	400	513	280
	180	KOH	0.20	100	136	4400
	180	KOH	0.20	200	274	3170
	180	KOH	0.20	300	409	1850
	180	KOH	0.20	400	568	1570
	180	KOH	0.050	400	605	460
	180	KOH	0.098	400	578	830
	180	KOH	0.39	400	548	2190
$Mo(CO)_6$	160	KOH	0.20	100	121	730
	160	KOH	0.20	200	269	400
	160	KOH	0.20	300	410	300
	160	KOH	0.20	400	540	220
	160	KOH	0.098	400	565	120
	160	KOH	0.39	400	495	250
$W(CO)_6$	140	KOH	0.20	100	145	160
	140	KOH	0.20	200	255	95
	140	KOH	0.20	300	435	70
	140	KOH	0.20	400	540	40
	160	KOH	0.20	100	102	1050
	160	KOH	0.20	200	250	570
	160	KOH	0.20	300	390	260
	160	KOH	0.20	400	565	270
	160	KOH	0.098	400	572	150
	160	KOH	0.39	400	536	440
	160	$NaHCO_2$	0.098	400	578	135
	160	$NaHCO_2$	0.20	400	580	240
	160	$NaHCO_2$	0.39	400	585	400
	160	$NaHCO_2$	0.78	400	592	560
	160	$N(C_2H_5)_3$	0.20	400	590	270
	160	$N(C_2H_5)_3$	0.39	400	525	445
	160	$N(C_2H_5)_3$	0.78	400	480	590

[a] Gauge pressure measured at room temperature ~25 °C. [b] Solution: 200 mL of 25% H_2O–75% CH_3OH mixture containing 0.126 mmol of transition metal carbonyl.

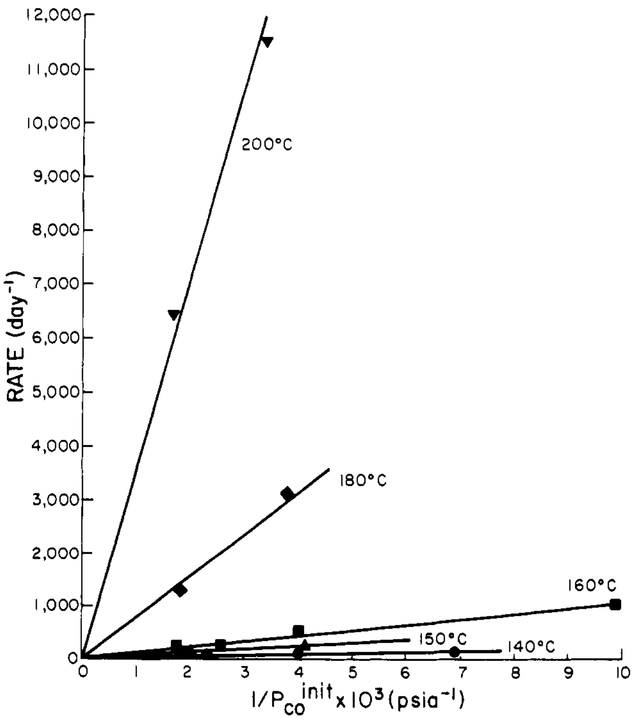

Figure 3. Rate of H_2 production by catalyst system containing $W(CO)_6$ measured at constant base concentration as a function of $1/P_{CO}^{init}$. Catalyst solution: $W(CO)_6$ (0.126 mmol), KOH (39 mmol), 25% H_2O–75% CH_3OH (200 mL).

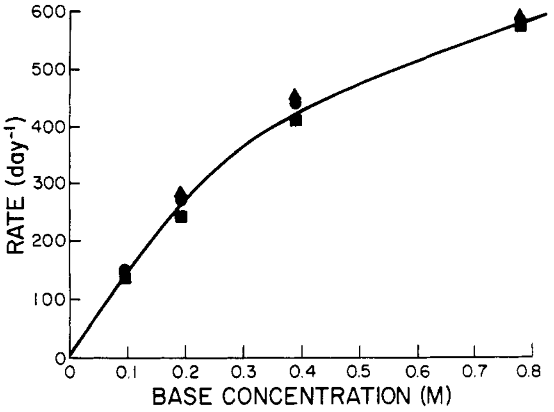

Figure 4. Rate of H_2 production measured at a constant CO loading pressure of 400 psig as a function of base concentration. Catalyst solution: $W(CO)_6$ (0.126 mmol), 25% H_2O–75% CH_3OH (200 mL). Temperature: 160 °C. ●, KOH; ■, $NaHCO_2$; ▲, $N(C_2H_5)_3$.

rate data fall on a common curve reinforces the point made earlier, namely that the actual base species present in these solutions is the formate ion and that at constant CO pressure and catalyst concentration it is this species that serves to control the rate of reaction. The rates of H_2 production with the use of $Cr(CO)_6$ and $Mo(CO)_6$ increase with KOH concentration in a similar fashion.

Table III lists the rates of hydrogen production measured at temperatures ranging from 130 to 200 °C for the group 6 transition metal carbonyl systems with the use of a solvent system of constant composition and two carbon monoxide loading pressures. The data for $W(CO)_6$ are shown as a van't Hoff plot in Figure 5. It is seen that the data describe a set of parallel lines whose slopes correspond to an activation energy of 32 kcal mol^{-1}. The rate data for $Cr(CO)_6$ and $W(CO)_6$ provide van't Hoff plots of

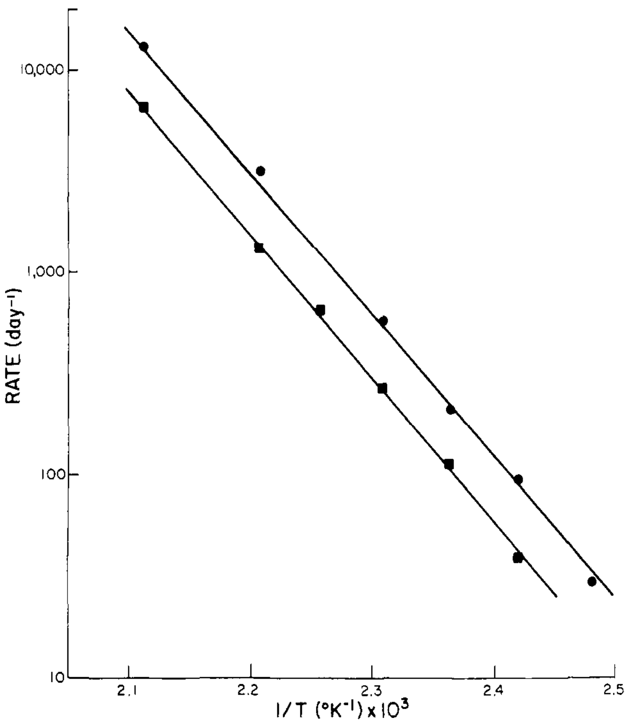

Figure 5. Rate of H_2 production by catalyst system containing $W(CO)_6$ at CO loading pressures of 200 and 400 psig plotted logarithmically as a function of reciprocal temperature. Catalyst solution: $W(CO)_6$ (0.126 mmol), 25% H_2O–75% CH_3OH (200 mL), KOH (39 mmol). ■, CO loading pressure = 200 psig; ●, CO loading pressure = 400 psig.

similar quality yielding an activation energy of 35 kcal mol^{-1} for both $Cr(CO)_6$ and $Mo(CO)_6$. A least-squares analysis indicates that the standard deviation for these activation energies is 0.8 kcal/mol.

The liquid phase of these wgs reaction systems has been examined under typical operating conditions ($P_{CO} \approx 580$ psia, $T = 140$ °C) with the use of an autoclave-infrared cell (spectraclave) developed in this laboratory.[6] Butanol–water mixtures containing dissolved KOH were used for these measurements since this solvent system has superior optical properties, i.e., fewer solvent absorption bands, in the 2000 cm^{-1} spectral region of interest.[7] In each instance, only one ν_{CO} band was observed, that of the parent transition metal hexacarbonyls (found at 1980, 1980, and 1975 cm^{-1} for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively, in this solvent system) even though the wgs reaction was proceeding at a reasonable rate as determined by the buildup of the $\nu = 2340$ cm^{-1} band of dissolved CO_2.

A plausible mechanism can be put forth which explains the observed kinetics in terms of mononuclear metal carbonyl species as follows:

$$CO + OH^- \xrightarrow{\text{fast}} HCO_2^- \quad (4a)$$

$$M(CO)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(CO)_5 + CO \quad (4b)$$

$$M(CO)_5 + HCO_2^- \xrightarrow{k_2} M(CO)_5HCO_2^- \quad (4c)$$

$$M(CO)_5HCO_2^- \xrightarrow{k_3} HM(CO)_5^- + CO_2 \quad (4d)$$

$$HM(CO)_5^- + H_2O \xrightarrow{k_4} H_2M(CO)_5 + OH^- \quad (4e)$$

$$H_2M(CO)_5 \xrightarrow{k_5} M(CO)_5 + H_2 \quad (4f)$$

$$M = Cr, Mo, W$$

Table III. The Effect of Temperature on the Rate of Production of H_2[b]

catalyst	temp, °C	CO loading[a] pressure, psig	P_{CO}^{init}, psia	rate, day^{-1}
$Cr(CO)_6$	150	200	245	195
	160	200	261	650
	160	400	513	280
	170	200	290	1620
	170	400	586	735
	180	200	274	3170
	180	400	568	1570
	190	200	295	8530
	190	400	555	3790
	200	400	588	7870
$Mo(CO)_6$	160	200	269	400
	160	400	540	220
	170	400	560	510
	180	200	275	1840
	180	400	580	1360
	190	200	277	4990
	190	400	565	2660
	200	200	294	12200
	200	400	552	6590
$W(CO)_6$	130	200	240	30
	140	200	255	95
	140	400	540	40
	150	200	242	210
	150	400	499	115
	160	200	250	570
	160	400	565	270
	170	400	554	650
	180	200	263	3140
	180	400	550	1310
	200	200	293	11500
	200	400	600	6500

[a] Gauge pressure measured at room temperature ~25 °C.
[b] Solution: 200 mL of 25% H_2O–75% CH_3OH mixture containing KOH (39 mmol, 0.20 M) and 0.126 mmol of transition metal carbonyl).

Here step 4a represents the very fast reaction observed in these systems by which the reaction of CO with OH^- forms the initial amounts of formate ion at the beginning of the wgs reaction and replenishes the supply of this ion as it is consumed in the catalytic cycle represented by steps 4c–f. A dissociative step 4b to form the pentacarbonyl metal species is invoked to explain the observed first-order behavior of the wgs reaction on the metal hexacarbonyl and the inverse pressure dependence observed with this reaction. Dissociative reactions such as this are commonly observed in ligand substitution reactions which are generally found to proceed by an S_N1 type dissociative mechanism.[8-11] The competition of CO (step 4b) and formate ion (step 4c) for the metal pentacarbonyl species explains the observed inhibition by CO shown in Figures 2 and 3, as well as the increase in rate of the wgs reaction with formate ion concentration seen in Figure 4. The pentacarbonyl metal formate anion of step 4c has been synthesized in the form of a bis(triphenylphosphine)iminium (Ppn) salt in this laboratory. Details concerning the synthesis and thermal decomposition of this salt will be described subsequently. A group 6 transition metal carbonyl dihydride such as that invoked in steps 4e and 4f has never been isolated. However indirect evidence for the existence of the species $H_2Cr(CO)_5$ has been reported.[12] Furthermore, the closely related trimethyl phosphite complex $H_2Cr[P(OCH_3)_3]_5$ has been recently characterized.[13] The thermal dissociation of $H_2M(CO)_5$ completes the catalytic cycle by regenerating the

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transition metal pentacarbonyl intermediate.

By applying the steady state approximation to steps 4b–f, one obtains the following rate expression:

$$\text{rate} = \frac{d[H_2]}{dt} = \frac{k_1 k_2}{k_{-1}} \frac{[M(CO)_6][HCO_2^-]}{[CO]} \tag{5}$$

By equating the concentration of dissolved CO to pressure through Henry's law, $[CO] = K_H(CO)P_{CO}$, one obtains an expression for the rate of H_2 production, which in terms of turnover number becomes:

$$\text{rate (day}^{-1}) = \left(\frac{k_1 k_2}{k_{-1} K_H(CO)} \right) \frac{[HCO_2^-]}{P_{CO}} \tag{6}$$

Thus this mechanism predicts that the wgs reaction should be first order in transition metal hexacarbonyl, first order in formate ion concentration, and inverse first order with respect to CO. Each of these predictions is borne out by the experimental data although the base dependence seen in Figure 4 deviates from linearity quite markedly at high concentrations. Considering the high formate salt concentrations and solvent system, it is likely that the curvature observed in Figure 4 reflects changes in formate ion activity brought about by classical ionic strength effects as well as ion pair equilibira.

The key steps in the reaction sequence proposed in eq 4 are the thermal decomposition of the formato anion $M(CO)_5HCO_2^-$ to produce CO_2 and H_2 in the presence of water (steps 4d–f). Accordingly, a series of experiments were performed to examine the thermal stability and degradation products of the Ppn salt of the tungsten pentacarbonylformato anion. The Ppn salt of $W(CO)_5HCO_2^-$ was synthesized by reacting $(Ppn)_2(W_2(CO)_{10})$ with silver formate according to the method of R. B. King, Ruff, et al.[14] The resulting light yellow $PpnW(CO)_5\ HCO_2$ salt was characterized by its IR spectrum which showed three bands at 1900 (vs), 1840 (s), and 1620 (m) cm^{-1} in KBr and 1910 (vs), 1840 (m), and 1610 (m) cm^{-1} in CH_2Cl_2; (literature value:[14] 1900 (s), 1837 (m), and 1612 (m) in CH_2Cl_2). In the first experiment a small sample of $PpnW(CO)_5HCO_2$ was placed in a clean 100-mL flask which was subsequently evacuated and flushed with argon. The dry salt was then gradually heated in an oil bath to 110 °C. The only gaseous product observed from the resulting decomposition of the anhydrous $PpnW(CO)_5HCO_2$ was CO_2. The second experiment was identical with the first except that a solution of $PpnW(CO)_5HCO_2$ in a 4:1 (v/v) mixture of 1-butanol–water was heated under an argon atmosphere. The thermal decomposition of $PpnW(CO)_5HCO_2$ in this aqueous medium was found to generate both H_2 and CO_2 in accordance with the postulated mechanism. Similarly, the thermal decomposition of $PpnW(CO)_5HCO_2$ was monitored by using IR spectroscopy in the spectraclave under elevated CO pressures (P_{CO} = 45 atm). Upon thermal decomposition in anhydrous 1-butanol at ~90 °C, the $PpnW(CO)_5HCO_2$ was found to revert to $W(CO)_6$ as indicated by the disappearance of the strong 1925-cm^{-1} band of the (formato)pentacarbonyltungstate annion and concomitant appearance of the 1975-cm^{-1} band of $W(CO)_6$. A very weak band appeared at 2340 cm^{-1} indicating the presence of CO_2 at a very low concentration. Identical results were obtained with a 4:1 (v/v) mixture of 1-butanol and water. In this case however the 2340-cm^{-1} band of CO_2 became progressively stronger throughout the experiment indicating that the wgs reaction was proceeding. These spectral observations are also in accord with the mechanism of eq 4.

Finally, since the ratio of rate constants k_1/k_{-1} in eq 6 is the equilibrium constant, K_{eq}, for the dissociation $M(CO)_6 \rightleftharpoons M(CO)_5 + CO$ (M = Cr, Mo, W), the apparent rate constant for the reactions studied here can be expressed as: $k = K_{eq}k_2/K_H(CO)$. It follows that each activation energy derived from this data is the sum of the enthalpy of dissociation for the metal hexacarbonyl, $\Delta H°$, the activation energy for step 2, $E_a(2)$, and the heat of solution of CO in the alcohol–water mixture, ΔH_s; $E_A = \Delta H° + E_a(2) - \Delta H_s$. The heat of solution for CO in an alcohol-rich solution is likely to be small and negative (the order of a few kcal/mol). Similarly, the activation energy associated with the addition of a ligand to a vacant bonding site is likely to be small. Thus one expects the dominant contribution to the activation energy to be the enthalpy of dissociation for $Mo(CO)_6$. It is interesting therefore to note that although they differ in trend, the activation energies obtained here, 35, 35, and 32 kcal/mol for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively, are similar in magnitude to the mean metal–CO bond dissociation energies reported by Cotton et al.[15] of 27.1, 35.9, and 42.1 kcal/mol for the respective metal hexacarbonyls. Alternatively, the activation energies obtained here can be compared to those measured for ligand substitution reactions. Werner and Prinz report values of 38.7, 30.8, and 39.6 kcal/mol for the activation energy associated the replacement of CO by triphenylphosphine for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively. Again, although the ordering differs, the activation energies obtained here are very similar in magnitude to those associated with the dissociation of a group 6 transition metal–CO bond.

Conclusion

Group 6 transition metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been shown to be catalyst precursors for the water gas shift reaction operating at temperatures ranging from 130 to 200 °C with the use of CO gas and water dissolved in methanol as reagents. The three transition metal carbonyls are found to have very similar catalytic activities. The rate of H_2 production is found to be first order in metal hexacarbonyl, increasing with base concentration, and inversely proportional to CO pressure, with activation energies that fall in the range 32–35 kcal/mol. The measured pH of the solutions is found to be quite low varying from 8.6 to 7.5 during the course of the reaction. A mechanism is proposed which invokes the catalytic decomposition of formate ion in a catalytic cycle in which the transition metal pentacarbonyl resulting from the thermal dissociation of the metal hexacarbonyl plays the active role of catalyst.

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