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Mechanistic Studies of the Homogeneous Catalysis of the Water Gas Shift Reaction by Rhodium Carbonyl Iodide

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Abstract: The water gas shift reaction, $H_2O + CO = H_2 + CO_2$, is effectively catalyzed at low temperatures and pressures by a catalyst system based on rhodium carbonyl iodide. The results of semiquantitative kinetic studies and of quenching experiments are reported. In the temperature range 80–100 °C the catalytic reaction shows first-order dependence on the partial pressure of CO and inverse dependence on acid and iodide concentrations. The major species in solution are rhodium(III) carbonyls. However, below 65 °C the reaction is independent of CO pressure, and exhibits second-order dependence on iodide concentration and positive dependence on acid concentration. Rhodium(I) species now become predominant in solution. The temperature dependence of the rate shows corresponding behavior. Above 80 °C the Arrhenius plot is linear with a slope which yields an apparent activation energy of 9.3 kcal mol^{-1}. However, below 70 °C it is concave downwards with a slope at 55 °C corresponding to 25.8 kcal mol^{-1}. Limiting behavior is not reached on the low-temperature side. These results are explained in terms of a change in the rate-limiting step of the catalysis. At high temperature CO_2 production from reduction of Rh(III) species by CO is viewed as rate determining, while at lower temperature hydrogen production from oxidation of Rh(I) species by protons is thought to be limiting. Possible intermediates are discussed and a mechanistic scheme is proposed. A steady-state kinetic analysis and assumptions about rate-determining steps show the mechanism to be consistent with the observed behavior of the system.

Introduction

The water gas shift reaction

$$H_2O + CO = H_2 + CO_2 \qquad (1)$$

has been known and studied for over 75 years. Its significance derives from its role in the preparation of ammonia synthesis gas[1] and from its ability to increase the H_2:CO ratio in gaseous feedstock for methanation and Fischer–Tropsch synthesis.[2] Its importance for the reduction of nitrogen and sulfur oxides in the treatment of combustion exhausts has also been recognized.[3]

Thermodynamically, the reaction is favored and slightly exothermic under ambient conditions ($\Delta H°_{298} = +0.68$ kcal mol^{-1}; $\Delta G°_{298} = -4.76$ kcal mol^{-1}). But, like most reactions of this type, kinetic barriers are large and the reaction only proceeds at useful rates at elevated temperatures, even with the available catalysts. Commercial catalysts for (1) are based mainly on either Fe_3O_4 and related oxides or on copper and copper-zinc oxide mixtures.[1] Both types of systems are heterogeneous, and operate at temperatures of 300–350 and 200–250 °C, respectively. However, because the equilibrium constant for (1) exhibits a negative temperature dependence, there exist at these temperatures significant equilibrium concentrations of both reactants and products. Thus, catalysis of (1) at lower temperatures is a desirable objective.

Attempts to catalyze the shift reaction homogeneously can be traced back to studies by Hieber[4] in 1932 on iron carbonyl, carbonyl hydrides, and carbonyl hydride anions. The reaction of $Fe(CO)_5$ with aqueous base was observed to result in the oxidation of CO to CO_2 and the reduction of H^+ to coordinated hydride. Further reaction of the product CO_2 with base produced carbonate. Acidification of the $HFe(CO)_4^-$ produced resulted in the formation of an unstable dihydride which liberated hydrogen. Regeneration of the starting complex by CO addition completed the cycle, and the water gas shift reaction was achieved in principle. The problem, however, was that (2) required strong base which was consumed stoichiometrically in the catalytic cycle. Further studies[5] produced no solution to this problem until recently, when Ford and co-workers[6] were able to catalyze (1) homogeneously using $Ru_3(CO)_{12}$ in alkaline ethoxyethanol. The rates of the reaction are slow, but stoichiometric base consumption is avoided because the $KHCO_3$ produced is unstable in ethoxyethanol under the reaction conditions, and decomposes to give CO_2 and the starting base, KOH. Subsequent to Ford's initial report, he and others[7-9] have described successful catalysis of (1) using a variety of metal carbonyls and carbonyl cluster compounds in basic media. In addition Pettit and co-workers[8] and Laine[10] have observed hydroformylation with these same catalyst systems, and an earlier patent by Fenton[11] describes shift catalysis using ammonia and amines as the base under more forcing conditions (56 atm CO and 200 °C).

$$Fe(CO)_5 + 2OH^- \rightarrow HFe(CO)_4^- + HCO_3^- \qquad (2)$$

Our interest in homogeneously catalyzing the water gas shift reaction derives from several notions. First, the reaction is

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relatively simple, and precedents for component parts of the reaction using metal complexes are abundant in the literature. Equation 3 represents the well-known reduction of metal ions by carbon monoxide,[12] and eq 4 corresponds to proton reduction by relatively basic metal ions.[13] The problem of catalyzing (1) then reduces to one of finding a system in which M and M′ are related, and eq 3 and 4 are readily compatible. Second, because of the simplicity of the shift reaction, its catalysis can serve as a model for activating CO toward reduction, which is more difficult to catalyze homogeneously. This is true despite the fact that (1) involves CO oxidation and neither C–C nor C–H bond formation, because in both cases oxidation-state changes at carbon require attack on that position. Third, homogeneous catalysis is usually carried out under mild conditions including relatively low temperature.

$$M^{n+} + CO + H_2O \rightarrow M^{(n-2)+} + CO_2 + 2H^+ \qquad (3)$$

$$M'^{n+} + H^+ \rightarrow H\text{—}M'^{(n+2)+} \xrightarrow{H^+} M'^{(n+2)+} + H_2 \qquad (4)$$

In our laboratory we have focused on developing catalyst systems that would operate in acidic media. Our initial report of water gas shift catalysis described a catalyst system formed from $[Rh(CO)_2Cl]_2$, aqueous HI, and glacial acetic acid.[14] When this catalyst system was charged with 250–400 Torr of CO at 80–90 °C, reaction 1 was observed to proceed. More recently, we have described a completely different catalyst based on platinum chloride–tin chloride chemistry, and have discussed the mode of catalysis for this system in terms of "coupled cycles".[15] In the present paper, we examine in depth the rhodium carbonyl iodide catalyst for (1), including kinetic studies, the identification of possible reaction intermediates, and a discussion of the mechanistic possibilities of this catalyst system.

Researchers at Monsanto have also been interested in the catalytic properties of the rhodium carbonyl iodide system in acidic media, and have used this system in their acetic acid process.[16,17] However, these workers reported the *absence* of any water gas shift products in their reactions of CO with methanol using the rhodium catalyst system.[17] Subsequent to the submission of this paper, their first report of water gas shift catalysis in aqueous acetic acid using the rhodium system has appeared.[18] Although the Monsanto study was conducted under much higher temperature and pressure conditions, many of their observations agree with ours and lead to similar conclusions. However, some significant differences were also found and these will be commented on where appropriate.

Experimental Section

General Methods and Materials. Rhodium trichloride hydrate (Matthey Bishop), tetraphenylarsonium chloride (Ventron), and carbon monoxide (Matheson) were used as purchased. All other materials were of reagent grade. Concentrated HCl refers to a 37% aqueous solution and concentrated HBF_4 refers to a 48% aqueous solution.

A Hewlett-Packard 5700A gas chromatograph with a thermal conductivity detector was used for analysis of gas mixtures. Gas samples were taken with a Pressure-Lok air-tight gas syringe (Series A-2) obtained from Precision Sampling Corp. Infrared spectra were recorded as either KBr pellets or in solution using CaF_2 cells on a Perkin-Elmer 467 grating infrared spectrophotometer.

The apparatus used in the kinetic studies consisted of a single-neck round-bottom flask connected via a side arm to a three-way stopcock. One stopcock lead was connected to either vacuum or a gas source, and the second lead was cut short, stoppered with a serum cap, and used for gas sampling. A ground glass adaptor connected the vessel to a mercury manometer. Solutions were immersed to the level of the side arm (at least 3 cm above the level of the solution) in an oil bath, stirred with a magnetic stirrer, and heated to a constant temperature using a heating element connected via a contact thermometer to a mercury relay. A second, calibrated thermometer was used to determine the actual temperature of the bath. The temperature variation of the bath was estimated as ±¼ °C. Blank runs with a thermometer immersed in the solution inside the flask showed the solution temperature to be a few degrees less than the bath temperature, the exact amount depending on the bath temperature. The recorded temperature in all experiments is the temperature of the bath.

Separation of diatomic gases (H_2, N_2, O_2, CO) was achieved on a molecular sieve 5A column (2 ft × 0.25 in.), and a Porapak Q column (12 ft × 0.125 in.) was used to separate H_2, CO, CH_4, and CO_2 for kinetic runs. Both columns were purchased prepacked from Hewlett-Packard, and helium was used as the carrier gas. The Porapak column was calibrated by connecting an empty reaction vessel to a mercury manometer and purging with the desired gas several times. The vessel was then filled with the gas, the system pressure recorded, and a 0.50-mL gas sample analyzed by GC. System pressure was reduced by momentary application of vacuum, another sample taken, and the process repeated. The gas pressure was taken as the difference between the vacuum pressure reading and the system pressure reading. To avoid spurious results at low pressure, the total pressure was kept above 300 Torr by diluting with a second gas when necessary, and the gas pressures were calculated assuming ideal mixing. Linear plots of peak height vs. partial pressure were obtained for CO, CO_2, and CH_4. The H_2 plot was nonlinear as expected when He serves as the carrier gas. All plots were checked several times and were reproducible to ±2%.

Preparation of Complexes. The dimer $[Rh(CO)_2Cl]_2$ was prepared by the method of McCleverty,[19] recrystallized from hexane, and stored in a desiccator. The $[Rh(CO)_2I_2]^-$ and $[Rh(CO)I_4]^-$ anions were prepared as their tetraphenylarsonium salts by the methods of Vallarino,[20] and the anions $[Rh(CO)_2I_4]^-$ and $[Rh(CO)I_5]^{2-}$ were prepared as their tetraphenylarsonium or tetra-*n*-butylammonium salts by the methods of Forster.[21]

Kinetic Runs. Stock solutions were prepared by diluting 83.3 mL of concentrated HCl or 23.6 mL of H_2O to 100 mL with glacial acetic acid. A weighed amount of sodium iodide was dissolved in 10.0 mL of H_2O followed by the addition of 5.0 mL of the aqueous stock solution and 10.0 mL of the HCl stock solution via pipet. The resulting mixture was quickly filtered through a coarse filter into a 50-mL volumetric flask. The sodium chloride precipitate was washed several times with small portions of acetic acid and the washings were added to the flask. The solution was then diluted to the mark with acetic acid and poured into a 500-mL reaction vessel containing a weighed amount of rhodium as $[Rh(CO)_2Cl]_2$. This resulted in a standard solution that was 2 M in acid and 20 M in H_2O, and this was held constant for all kinetic runs. The standard total rhodium and iodide concentrations were 0.01 and 2 M, respectively, although this was varied for specific runs.

After preparation the system was degassed, filled with carbon monoxide, and heated at 80 °C until CO_2 and H_2 began to appear in the GC. This resulted in the reduction of any iodine formed by air oxidation of iodide and produced an active catalyst solution. This solution was degassed via several freeze-pump-thaw cycles, allowed to equilibrate to room temperature, and charged with CO and a small amount of CH_4 which served as an internal reference. The gases over the solution were sampled by GC to establish initial values of partial pressures. The solution was then immersed in the hot oil bath, and the gases were sampled periodically.

A single catalyst solution was used to study both the CO dependence and the temperature dependence and was degassed and recharged between runs. For the iodide dependence the procedure was modified by using concentrated HBF_4 instead of HCl and adjusting the amount of water appropriately, and by using a stock solution of $[Rh(CO)_2Cl]_2$ dissolved in acetic acid to maintain reproducibility in the rhodium concentration. Furthermore, since the solution could not be reused, the kinetic runs were scaled down to 10 mL of solution in a 100-mL reaction vessel.

Quenching Runs. An active catalyst solution was established as in the kinetic studies, cooled to room temperature, and stored under CO. Aliquots were removed and reheated under CO until CO_2 and H_2 appeared in the GC. An excess of tetraphenylarsonium chloride dissolved in a minimum of H_2O was injected via syringe into the hot solution and the solution was quickly cooled in an ice bath. Ice-cold water was injected to complete the precipitation, still under a CO atmosphere. When the liquor over the precipitate was clear, the precipitate was filtered and washed in air, dried under vacuum, and examined by IR both in the solid state and dissolved in nitromethane.

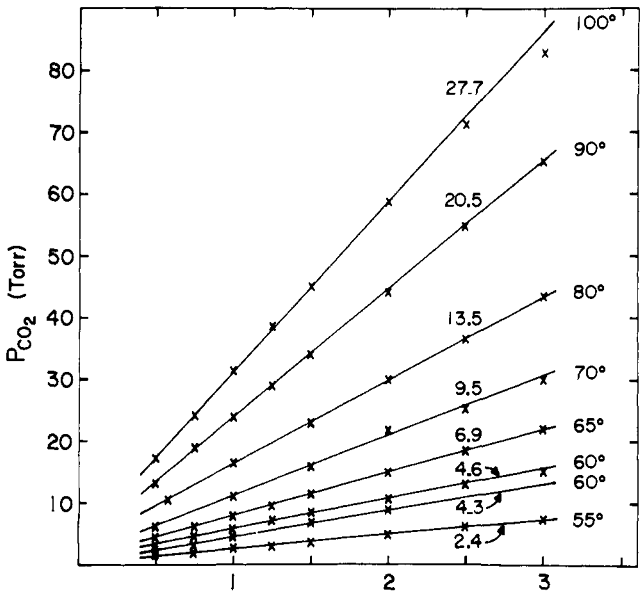


Figure 1. Rates of CO_2 production by water gas shift (WGS) catalysis at various temperatures.

Table I. Water Gas Shift Catalysis at Different Rhodium Concentrations[a]

run	$[Rh]_t$,[b] M	temp, °C	rate, Torr/h[c]
1A	0.0051	80	3.3
1B	0.0102	80	6.1
1C	0.0203	80	11.7
2A	0.0102	60	4.3
2B	0.0204	60	8.6

[a] $[H^+] = [I^-] = 2$ M; $[H_2O] = 20$ M; $P_{CO} = 435$ Torr. [b] The total concentration of all rhodium species. [c] The rates in this and other tables have an estimated standard deviation of 0.1 Torr.

Results and Discussion

The chemistry on which homogeneous catalysis of the water gas shift reaction is based is well known, as previously pointed out. Carbon dioxide formation in eq 3 undoubtedly proceeds via a sequence involving CO coordination to a metal ion in a higher oxidation state, followed by nucleophilic attack of water at carbon, and reductive decarboxylation. Activation of CO toward nucleophilic attack is enhanced by the reduced M → CO back-bonding from the higher oxidation state metal ion. James et al.[22] have demonstrated CO_2 production from a Rh(III) carbonyl, as shown in the equation

$$Rh^{III}(CO) + 2CO \xrightarrow{H_2O} Rh^{I}(CO)_2 + CO_2 + 2H^+ \quad (5)$$

The formation of hydrogen from protons, eq 4, has been less widely observed. However, oxidative addition of HX to Rh(I) systems is well established,[23] and the reaction of $Rh(CO)_2I_2^-$ with HI has been reported by Vallarino[20] and Forster[21] to give hydrogen, as seen in the equation

$$Rh(CO)_2I_2^- + 2HI \rightarrow Rh(CO)I_4^- + H_2 + CO \quad (6)$$

By combining these two reactions, (5) and (6), a catalytic cycle for (1) can be envisaged, and was in fact realized in our initial report of water gas shift catalysis. Despite the precedents, however, relatively little could be said at that time about the mechanism of the catalysis, since only limited mechanistic information was available for CO_2 formation via eq 5 and none for H_2 formation via eq 6. Thus the present studies were undertaken in the hope of shedding light on the intimate nature of the catalysis.

Semiquantitative kinetic investigations were carried out by the method of initial rates. The gas mixture above the catalytic solution was periodically sampled by gas chromatography. The peak heights were corrected to their room temperature values using an internal methane standard and converted to partial pressures by means of a calibration plot. Both the disappearance of CO and the appearance of H_2 and CO_2 were monitored. All three showed the same initial rates within experimental error. Since the thermal conductivity detector of the gas chromatograph showed the greatest sensitivity and best reproducibility for CO_2, its appearance was used as the measure of the rate in all calculations. Experimentally the pressure increase of CO_2 was observed to be linear with time for the first few hours of the reaction as shown in Figure 1. The slope of this linear portion, as determined by a least-squares fit of the data, was taken as the initial rate.

The dependence of the rate on rhodium concentration was determined by adding an additional weighed portion of $[Rh(CO)_2Cl]_2$ to the catalytic solution between runs, followed by degassing and recharging with CO. The results are given in Table I. A plot of log $(\Delta P_{CO_2}/\Delta t)$ vs. log $[Rh_{total}]$ for the data at 80 °C is linear with a slope of 0.92, indicative of first-order dependence on the total rhodium concentration. The slight deviation from a value of 1.0 is probably due to small losses in the transfer of the weighed $[Rh(CO)_2Cl]_2$ to the reaction flask and no significance is attached to it. The data at 60 °C show a similar first-order dependence. These results, when combined with the quenching experiments discussed below, which show only mononuclear rhodium complexes, prove that the catalytically important species in the temperature range studied are mononuclear. This conclusion of strictly "mononuclear" chemistry is consistent with the known chemistry of rhodium carbonyl halides in the presence of excess halides.[24] It is clear, then, that homogeneous catalysis of (1) by the rhodium carbonyl iodide system does not involve or require clusters or polynuclear units under our reaction conditions.

The effect on the rate of altering the partial pressure of CO was also investigated. To avoid changes in concentration between runs a single solution was used which was 0.01 M in rhodium, 2 M in H^+ and I^-, and 20 M in H_2O. (Some water will be consumed in each run, but it is an amount corresponding to a negligible portion of the total present.) The solution was degassed and recharged between runs, and the initial run repeated at the end to be sure no significant changes had occurred. Runs 3C and 3D contained nitrogen in addition to CO to keep the total pressure high enough to avoid sampling errors. Again, product evolution was observed to be linear with time for several hours and slopes of ΔP_{CO_2} vs. Δt were used as a measure of the rate. The results at both 80 and 100 °C are given in Table II. At 80 °C a plot of log $(\Delta P_{CO_2}/\Delta t)$ vs. log $[P_{CO}(\text{initial})]$ is linear with a slope of 1.0. Furthermore, run 3B was allowed to proceed to approximately 50% of completion as measured by the decrease in P_{CO}, and a plot of log $[P_{CO}(\text{initial})/P_{CO}]$ vs. time is linear. This clearly establishes a first-order dependence on P_{CO} at this temperature. However, at 100 °C the corresponding log-log plot of rate vs. P_{CO} is nonlinear, with the slope changing from about 1 at 400 Torr to nearly 1.2 at 65 Torr of CO. This change is much greater than experimental error and the significance of this observation is discussed further below.

The temperature dependence of the reaction was examined using the same solution charged to a pressure of ~400 Torr of CO. The results are listed in Table III and shown graphically in Figure 1. Small differences in the initial CO pressure were unavoidable, and the rates were corrected to 400 Torr of CO assuming first-order dependence on CO. Examination of the data showed that the logarithm of the rate was not linear with

Table II. Water Gas Shift Catalysis at Different CO Pressures

run	P_{CO}, initial, Torr	temp, °C	rate, Torr/h	turnovers/h^c
3A^a	449	80	16.1	0.83
3B	242	80	8.6	0.44
3C	145	80	5.4	0.28
3D	68	80	2.5	0.13
4A^a	381	100	27.7	1.42
4B	207	100	15.0	0.77
4C	168	100	12.3	0.63
4D	66	100	4.0	0.21
6A^b	600	80	3.4	0.17
6B	295	80	3.5	0.18

[a] $[H^+] = [I^-] = 2$ M; $[H_2O] = 20$ M; $[Rh]_t = 0.01$ M. [b] Same except $[I^-] = 0.5$ M. [c] Calculated as mol CO_2/mol catalyst using the measured gas-phase volume of 480 mL and a solution volume of 50 mL.

Table III. Water Gas Shift Catalysis at Different Temperatures^a

run	temp, °C	P_{CO}, initial, Torr	rate, Torr/h	rate$_{cor}$, Torr/h
5A	100	381	27.7	29.1
5B	90	397	20.5	20.6
5C	80	369	13.5	14.7
5D	70	398	9.5	9.6
5E	65	412	6.9	6.9
5F	60	386	4.3	4.3
5G	60	625	4.6	4.6
5H	55	422	2.4	2.4

[a] $[H^+] = [I^-] = 2$ M; $[H_2O] = 20$ M; $[Rh]_t = 0.01$ M. [b] Data above 70 °C corrected to 400 Torr assuming first-order P_{CO} dependence.

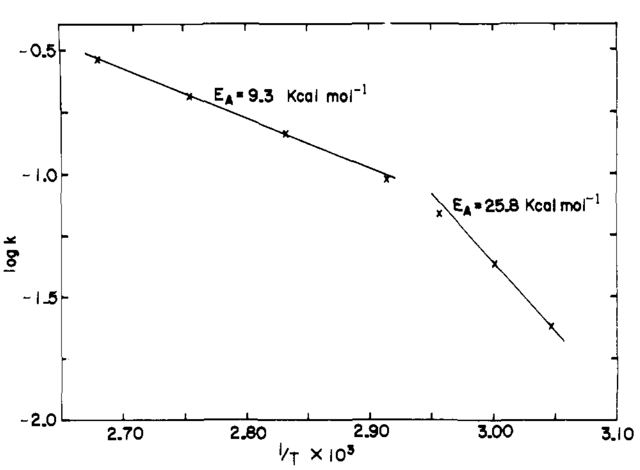


Figure 2. Arrhenius plot for WGS catalysis over the temperature range 55–100 °C.

Table IV. Catalytic Rates and Apparent Order in Iodide at Several Temperatures^a

		$[I^-]$, M				
		0.454		1.050		1.965
temp, °C	55			0.6	$\xrightarrow{2.1}$	2.2
	60	0.3	$\xrightarrow{2.0}$	1.6	$\xrightarrow{1.2}$	3.3
	80	2.0	$\xrightarrow{2.1}$	11.5	$\xrightarrow{-0.8}$	7.1
	90			18.4	$\xrightarrow{-1.0}$	9.7

[a] $[H^+] = 2$ M, $[H_2O] = 20$ M, $[Rh]_t = 0.01$ M, $P_{CO} = 400$ Torr. Rates are given in Torr/h and the apparent order in $[I^-]$ is shown on the arrow.

($1/T$) over the entire temperature range as expected, but only above 70 °C, the slope changing markedly below that temperature. Further investigation (run 5G) showed that at 60 °C the rate was essentially constant for a 1.6-fold increase in CO pressure, indicating a change in the kinetics. Figure 2 displays an Arrhenius plot of the data at 400 Torr of CO pressure, assuming that below 70 °C the rate is independent of P_{CO}. Above 70 °C the data are adequately fit by a straight line whose slope yields an apparent Arrhenius activation energy, E_a, of 9.3 kcal/mol.[25] At lower temperatures the slope becomes much steeper, but there are insufficient data to determine if it again becomes linear. Attempts to extend the temperature range below 55 °C were unsuccessful owing to the extreme slowness of the reaction. The slope between 55 and 60 °C yields an activation energy of 25.8 kcal/mol, which can be taken as a lower bound for the apparent activation energy of the low-temperature regime.

This unusual temperature dependence was perhaps the most intriguing and unexpected aspect of the present studies, and also the most revealing, as it enabled us to interpret preliminary results on iodide dependence. The Arrhenius plot, while linear at higher temperatures, is concave downwards in the region of changing kinetics. The plot appears to us as segmented, indicative of a change in the rate-determining step with changes in temperature. The more commonly discussed example of a segmented Arrhenius plot involves a change in the rate-limiting step between two competitive reactions.[26] However, this leads to a plot which is concave upwards, with the reaction path having the higher activation energy predominating at higher reaction temperatures. In the present situation, the reaction step (or sequence) having the higher activation energy "predominates" at lower reaction temperature—i.e., the step with the larger E_a is rate limiting at lower temperature, while the lower activation energy process becomes rate limiting in the higher temperature regime. This interpretation suggests that the change in the rate-limiting step occurs between consecutive reactions, and does not represent a case of two competing reaction paths. Concave downwards Arrhenius plots have been observed occasionally in inorganic reaction kinetics and have been similarly interpreted.[27] Catalytic cycles involving, as they must, consecutive reactions are more susceptible to this type of temperature dependence, and indeed it is sometimes observed in enzyme-catalyzed reactions.[28]

The Arrhenius plot should become linear again if an alternate step becomes rate determining. That it does not is presumably due to a lack of additional low-temperature data. Other factors, such as change with temperature of an equilibrium constant, can be responsible for curvature in an Arrhenius plot.[29] However, in the present case, concurrent changes in the kinetic orders and predominant species present, discussed below, favor our interpretation of a change in the rate-limiting step of the catalytic cycle.

The apparent change in kinetics around 65 °C was further confirmed by investigating the effects of altering the iodide concentration. Since chloride is known to replace iodide on rhodium complexes under some conditions,[24] HCl was replaced by HBF_4 for these experiments. Decreasing the amount of sodium iodide in the catalyst recipe then resulted in replacing I^- in solution by BF_4^-, thus maintaining the ionic strength. Preliminary data at 80 °C gave inconsistent results, and only after the importance of temperature was realized was the significance of these data recognized. Additional data were measured at several temperatures, and the results are shown in Table IV, where the apparent order for a given concentration change is also reported. Examination of the table reveals the change in the kinetics. At either low temperature or low iodide concentration the reaction is second order in iodide, while at high temperatures and the higher iodide concentrations first-order inhibition by iodide is observed. That the change in iodide kinetics is paralleled by the previously observed change in CO kinetics was confirmed by repeating run 3 (Table II) at an iodide concentration of 0.5 M. The results at two substantially different CO pressures are shown as run 6 of Table II. Whereas at a 2 M iodide concentration the catalysis is first order in CO pressure, at a 0.5 M iodide concentration, where the iodide kinetic dependence changes, the catalysis becomes independent of CO pressure.

Although both are necessary for the reaction, the effect of acid or water on the rate was not examined in any quantitative way because it was felt that unknown changes in activity coefficients would preclude useful measurements. However, it was observed qualitatively that increases in the acid concentration affect the rate positively at low temperature, but inversely at higher temperatures. The effect of water was too complicated to be analyzed. The kinetic dependences on CO, iodide, and acid concentrations thus change with temperature in accord with the segmented Arrhenius plot. In the case of iodide the change is by three powers. These results provide firm support for the notion of a change in the rate-limiting step of the catalysis, and not simply a shift in a prior equilibrium step.

To gain further insight into the reaction and identify possible intermediates, attempts were made to examine the infrared spectrum of the active catalytic solution. Unfortunately the large amount of water present completely obscured the carbonyl region of the spectrum. However, the reaction could be quenched in an ice bath and acetic anhydride added to remove the water. The resulting acetic acid solution showed a single stretch at 2092 cm^{-1} attributable to the *trans*-$Rh(CO)_2I_4^-$ anion.[30] This was true whether the quenching took place from 80 or 60 °C. Removing the acid instead of water from the active solution by adding sodium carbonate resulted in a color change from dark red to yellow and salts of $Rh(CO)_2I_2^-$ could be isolated.

The above observations suggested that both Rh(III) and Rh(I) species were important to the catalytic cycle. To explore this further the catalysis was quenched by injecting a bulky cation into the solution and then cooling in an ice bath. Immediate precipitation was noted, and it was completed by the addition of cold water. The resulting solid was isolated and examined by IR both in KBr pellets and nitromethane solution. Peaks in the carbonyl stretching region were compared both with known literature values[20,21,30] and directly with independently prepared samples of $Rh(CO)I_4^-$, $Rh(CO)I_5^{2-}$, *cis*- and *trans*-$Rh(CO)_2I_4^-$ and $Rh(CO)_2I_2^-$. No peaks were observed that were not accounted for by one of the above species, and thus possible intermediates were not detected. However, the distribution of the Rh species upon quenching from different temperatures was instructive. Above 80 °C, the infrared spectrum of precipitated solid displayed peaks at 2084 and 2035 cm^{-1} in KBr. These are attributed to *trans*-$Rh(CO)_2I_4^-$ and $Rh(CO)I_5^{2-}$, respectively. In the spectrum of solids precipitated from 100 °C the lower energy peak was considerably larger than the higher energy peak, while the reverse was observed when the precipitation occurred from 80 °C. In solution at room temperature these two species are in equilibrium with *cis*-$Rh(CO)_2I_4^-$, and the solution IR showed the five carbonyl stretches associated with these four anions.[31] The assignment was confirmed by observation of the enhancement of the $Rh(CO)I_4^-$ carbonyl stretch at the expense of the ν_{CO} of the dicarbonyl species upon standing in air, the reverse changes upon addition of CO to the solution, and the enhancement of the $Rh(CO)I_5^{2-}$ carbonyl stretch upon addition of I^- to the solution. There is no suggestion of any peak below 2000 cm^{-1} where Rh(I) dicarbonyl species would be expected to absorb.

In contrast, the precipitated solids from reactions run at temperatures below 80 °C showed peaks at 2040 and 1970 cm^{-1} in KBr or 2064 and 1989 cm^{-1} in solution due to $Rh(CO)_2I_2^-$. The $Rh(CO)_2I_4^-$ peak was still present and any other peaks were hidden under these strong absorptions. By decreasing the iodide concentration to 0.5 M, catalytic solutions could be obtained at low temperature that were nearly yellow in color, suggesting very little Rh(III), and from which only $Rh(CO)_2I_2^-$ could be precipitated. Raising the temperature caused the catalytic solution to darken appreciably.[32]

These experiments show that Rh(III) species predominate at higher temperatures while Rh(I) species are the major components at low temperatures. Coupled with the kinetic studies, we interpret these observations to mean that the limiting process at higher temperature, where the catalysis depends on CO pressure but is inverse in H^+ and I^- concentrations, is the reduction of a Rh(III) carbonyl with the release of CO_2. At low temperature, where Rh(I) predominates and the rate depends on H^+ and I^- concentrations but not on CO pressure, we suggest that the rate-limiting step is the oxidation of Rh(I) by HI with the release of H_2.

The recent report of the Monsanto group on water gas shift catalysis by rhodium carbonyl iodide,[18] carried out at 185 °C and 200-400 psi of carbon monoxide, confirms most of the above observations and extends support for the idea of different rate-limiting steps to a wider range of temperature and pressure conditions. In agreement with our results, Singleton et al. observe that Rh(III) species predominate when acid and iodide concentrations are high and Rh(I) species predominate when these concentrations are low. Although kinetic dependences were not determined quantitatively, they find that increased iodide decreases the rate of catalysis at higher acid (lower water) levels, but increases it at lower acid (higher water) levels, and that increasing the acid concentration at a constant iodide level first enhances, then inhibits, the reaction. This, too, agrees with the present study. Finally they propose, as we do, that at low acid and iodide levels oxidation of Rh(I) (H_2 formation) is rate determining, but at higher concentrations reduction of Rh(III) (CO_2 formation) becomes rate limiting. Although temperature was not varied systematically, they conclude from runs at 185 and 175 °C that the Rh oxidation step probably has a greater activation energy than the reduction step.

The rates of water gas shift catalysis obtained in the two studies under significantly different conditions are surprisingly consistent. If the rate of ~1 turnover/h obtained in the present study at 90 °C and P_{CO} of 400 Torr is extrapolated to 185 °C and 400 psig of CO assuming an activation energy of 9.3 kcal/mol and a first-order CO dependence, one obtains a rate of ~700 turnovers/h. This value is of the same magnitude as the ~400 turnovers/h rate reported by Singleton et al. However, at the higher CO pressures, Singleton et al. observe a kinetic independence of P_{CO} when Rh(III) reduction is rate limiting, and this change of kinetics may account for their smaller value (vide infra). Extrapolation of our rate data[33] also shows that the two kinetic regimes which we observed initially by temperature variation are both still accessible at 185 ° C and 400 psig. Hence Singleton et al.[18] were able to observe the same two rate-limiting regimes by varying the concentrations of iodide, water, and acid that we observed by $[I^-]$ and temperature variation in Table IV. The agreement between the two studies thus seems quite remarkable.

The principal difference between the Singleton et al. study and the present one occurs in the observations of CO dependence. They find that increasing P_{CO} inhibits the reaction in the regime where Rh(I) oxidation is rate limiting but that the reaction is independent of P_{CO} when Rh(III) reduction is limiting, whereas we find that the catalysis is independent of P_{CO} and first-order dependent in P_{CO} in those regimes, respectively. In view of the much higher temperatures and pressures of the Singleton study, it is possible that different steps in the catalytic pathway could change in relative importance, thus altering the kinetic dependence on P_{CO}. This is discussed further below.

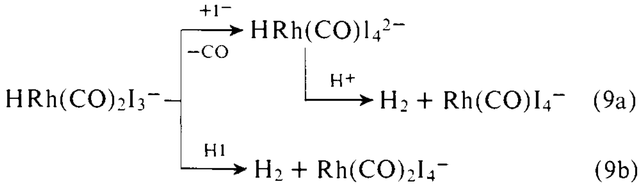
While lack of data about intermediates and individual reaction steps precludes a detailed kinetic analysis, the observed data can be accommodated by the scheme shown in Figure 3. Although rhodium is added in the form of $[Rh(CO)_2Cl]_2$ for convenience, in the presence of a large excess of iodide the species initially present is undoubtedly $Rh(CO)_2I_2^-$, since halide exchange is expected to be rapid and complete under these conditions.[24] Indeed, in the absence of strong acid, salts of $Rh(CO)_2I_2^-$ can be precipitated from the solution. Furthermore, as previously mentioned $Rh(CO)_2I_2^-$ has been observed to react with HI to produce hydrogen, other carbonyl halides being unreactive. Although we were unable to observe intermediates in this oxidation process, a rhodium hydride is likely involved. We propose that the rhodium(I) species can reversibly add HI to give a rhodium(III) hydride. Although it is more common in oxidative addition reactions for the electrophilic part of the substrate to react with the metal complex before the addition of the nucleophilic part, in this case we suggest that iodide addition may occur first, followed by protonation, as shown in eq 7 and 8. This proposal accounts

$$Rh(CO)_2I_2^- + I^- \rightleftarrows Rh(CO)_2I_3^{2-} \tag{7}$$

$$Rh(CO)_2I_3^{2-} + H^+ \rightleftarrows HRh(CO)_2I_3^- \tag{8}$$

for the requirement of a large excess of iodide in order to get observable rates, and also for the lack of reactivity of halides other than iodide, as the initial equilibrium is expected to lie far to the left even for iodide. Such a prior addition of halide has been proposed to explain the rates at which related oxidative additions occur.[34]

The hydride resulting from (7) and (8) is unobserved and presumably is present only at low concentration. A similar hydride was proposed by Forster[35] for the corresponding reaction of $Ir(CO)_2I_2^-$ with HI, and infrared absorptions at 2160, 2107, and 2056 cm⁻¹ were attributed to it, although the complex could not be isolated. In some of the quenching experiments we have observed a weak peak at 2150 cm⁻¹ which may be due to the hydride. Under catalytic conditions this hydride species is assumed to react with additional HI, based on the observation of a second-order iodide dependence in the kinetics at lower temperatures, and this latter reaction is thus proposed as the limiting step in hydrogen production. As shown in eq 9, the hydride could undergo a ligand exchange reaction, with I^- replacing CO, to give the highly basic species $HRh(CO)I_4^{2-}$. This would readily react with H^+, yielding H_2 and $Rh(CO)I_4^-$. Or the hydride could undergo a proton-assisted interchange of iodide and hydride ligands to yield H_2 and $Rh(CO)_2I_4^-$. Both these Rh(III) products are known and are interconvertible under a CO atmosphere.[21] In the absence of CO, only monocarbonyl species are observed and the reaction stops, with 1 mol of H_2 being evolved per mol of rhodium.[14] Precipitation under catalytic conditions reveals both mono- and dicarbonyl species, with the former increasing at higher temperature in accordance with a shift in the equilibrium.[36]



$$HRh(CO)_2I_3^- \begin{cases} \xrightarrow[-CO]{+I^-} HRh(CO)I_4^{2-} \xrightarrow{H^+} H_2 + Rh(CO)I_4^- & (9a) \\ \xrightarrow{HI} H_2 + Rh(CO)_2I_4^- & (9b) \end{cases}$$

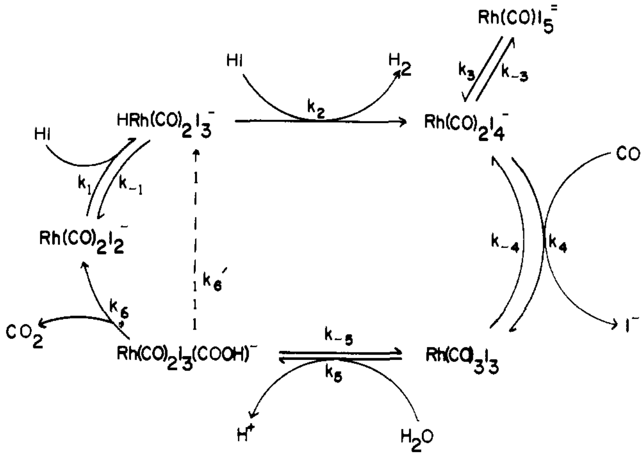


Figure 3. Proposed mechanistic scheme for WGS catalysis using rhodium carbonyl iodide.

While we observe kinetic independence of P_{CO} at 60 °C where H_2 formation is rate limiting, Singleton et al.[18] see inhibition by CO in this regime and they propose that path 9a is followed. Three possible reasons for the apparent discrepancy can be put forth: (1) under the drastically different conditions employed, different paths are followed—(9b) in the present study and (9a) in the Monsanto study; (2) our CO independence data (runs 5F and 5G) comprise an artifact—i.e., at 60 °C our system was still in the crossover region from first-order CO dependence to first-order CO inhibition (unfortunately at still lower temperatures the reaction was so slow as to preclude study); or (3) path 9a involves a concerted CO/I^- interchange not requiring prior dissociation of CO (i.e., an $\mathbf{I}_a$ mechanism[37]), thus altering the kinetic consequences of path 9a.[38]

The Rh(III) carbonyls produced above can in turn be reduced back to Rh(I) through the attack of water and subsequent release of CO_2 and protons. This process is seen as rate limiting at higher temperatures. The kinetics show this step to be inverse in acid and iodide concentrations, and directly proportional to the partial pressure of CO. The data for CO dependence at 80 and 100 °C, respectively, show clear first-order behavior at the lower temperature, but a slight trend toward a second-order contribution at the higher temperature and low CO pressures. Based on these results and the quenching experiments, we suggest that $Rh(CO)_2I_4^-$ is the predominant rhodium species present under catalytic conditions at 80 °C, and that it can react reversibly with CO to give $Rh(CO)_3I_3$:

$$Rh(CO)_2I_4^- + CO \rightleftarrows Rh(CO)_3I_3 + I^- \tag{10}$$

The equilibrium in (10) lies well to the left, and the tricarbonyl species is an unobserved, postulated intermediate which would be expected to have activated carbonyls.[39] At higher temperatures and lower CO pressures, more rhodium in the system would be expected to be present as monocarbonyl species, as evidenced by the increasing amount of $Rh(CO)I_5^{2-}$ in the quenching experiments. This would account for the observed tendency toward second-order dependence on the CO pressure at 100 °C. Reaction of the tricarbonyl with water would result in a hydroxycarbonyl complex for which there is considerable precedent.[40] This in turn can either lose CO_2 and HI to give $Rh(CO)_2I_2^-$ again, or remain in the rhodium (III) state by transferring the proton to the metal ion via a heteroatom β-elimination and continuing in the catalytic cycle as the hydride.

In the limit of Rh(III) reduction, the Monsanto group[18] observes independence of P_{CO} and they suggest direct attack of water on $Rh(CO)_2I_4^-$. This observation and conclusion are at variance with our results. If their results are correct, then Singleton et al.[18] should see independence of $[I^-]$ at strong acid (low water) levels but in fact they observe iodide inhibition as we do. Forster[18] explains this iodide inhibition in terms of an increase in acidity using the Hammett acidity function for the catalyst medium, but such an explanation will not yield the clean inverse first-order dependence which we observe in the limit of Rh(III) reduction. Clearly, experiments designed to probe the kinetic dependence of I^- at constant proton activity must be done to resolve this discrepancy.

The positive dependence on P_{CO} which we see and which Singleton et al.[18] do not is consistent with James' study[41] of the CO reduction of $RhCl_3$ in aqueous solutions via the nonautocatalytic route (the autocatalytic route is ruled out in the present study by the [Rh] kinetic dependence), and the proposed intermediate $RhI_3(CO)_3$ receives support from the isolation and characterization[17b,42] of $IrI_3(CO)_3$, which has an extremely high ν_{CO} (2185 cm^{-1}) suggestive of CO activated to nucleophilic attack. While this discrepancy in CO dependence is not resolved at this time, our results are internally consistent based on the scheme discussed below.

The rate data determined in the present study are catalytic rates measured under steady-state conditions, and yield no information about rate constants of individual steps. However, the observed kinetic dependences can be accounted for using the mechanism shown in Figure 3 in the following way. All of the rhodium species shown in the scheme are assumed present at steady-state concentrations, and steps involving the evolution of the product gases H_2 and CO_2 are assumed to be irreversible.[43] Following the procedures of King and Altman,[44] expressions for the steady-state distribution of rhodium among the various complexes can be obtained, and from them a complete rate law for the proposed mechanism can be derived. The distribution expressions and full steady-state rate law are given in the Appendix. While the full rate law has numerous terms, the observed kinetic dependences can be found to emerge readily by making certain simplifying assumptions.

When H_2 production is rate limiting, k_1 and k_2 can be assumed to be sufficiently smaller than the other rate constants so that terms involving them can be ignored in the denominator of the full rate expression. Moreover, if k_{-1} is taken as much larger than k_1 in comparing the remaining terms in the denominator, eq 11 results, which shows a second-order dependence on $[H^+]$ and $[I^-]$ and no dependence on P_{CO}. ([Rh] represents the total rhodium concentration.) While the analysis is an obvious oversimplification, as both steps 1 and 2 are probably each composed of more than one elementary process, the assumption of making the forward reactions of $Rh(CO)_2I_2^-$ with HI rate limiting, and the rate constant k_{-1} for the back reaction to Rh(I) very large, yields an expression which agrees with the low-temperature results.[45]

$$\text{rate} = \frac{k_1k_2}{k_{-1}}[\text{Rh}][\text{H}^+]^2[\text{I}^-]^2 \tag{11}$$

On the other hand, agreement with the high-temperature results is achieved when CO_2 production is taken as rate limiting.[46] In this case, k_6 is assumed to be sufficiently small so that terms involving it are dropped from the denominator, and in those terms remaining k_{-4} is assumed much larger than k_4; i.e., $Rh(CO)_3I_3$ is viewed as a highly unstable transient which readily returns to $Rh(CO)_2I_4^-$ if it does not react to form CO_2. A rate expression of the form shown in (12) then results, where K_{eq} is the equilibrium constant between di- and monocarbonyl Rh(III) species, k_3/k_{-3}.

$$\text{rate} = \frac{kP_{CO}^2[\text{Rh}][\text{H}_2\text{O}]}{[\text{H}^+][\text{I}^-]\{P_{CO} + [\text{I}^-]/K_{eq}\}} \tag{12}$$

As long as $[I^-]/K_{eq}$ is small relative to P_{CO}, a first-order dependence on P_{CO} results, but, as this term becomes larger, greater than first-order dependence should be seen. This term should also become more significant at higher temperatures and lower CO pressures, as the equilibrium shifts toward the monocarbonyl. Equation 12 thus predicts kinetic dependences which are roughly in accord with our observations.

Through this steady-state kinetic analysis we were able to reproduce the general features of the kinetics of catalyzing (1) by rhodium carbonyl iodide. The temperature dependence of the rate shows segmented behavior which can be explained in terms of a change in the rate-limiting step of the catalysis. At high temperatures (>80 °C) step 6 is rate limiting, while at low temperatures (<65 °C) step 2 becomes rate determining. The required large magnitudes of k_{-4} and k_{-1} in these two temperature regimes, respectively, are consistent with the absence of observable intermediates and with our chemical intuition, and lead to the emergence of the observed kinetic orders. Moreover, when k_6 is rate limiting, quenching of the catalysis should produce $Rh(CO)_2I_4^-$ and $Rh(CO)I_5^{2-}$ as the stable rhodium species, whereas, when k_2 is rate limiting, significant amounts of $Rh(CO)_2I_2^-$ should be present, and again this is in agreement with our observations.

One final curious result which comes out of the kinetic analysis pertains to CO_2 production via heteroatom β-elimination, which is represented in Figure 3 as step 6′. If this path is followed, the catalytic cycle never leaves the Rh(III) regime. However, when H_2 production is rate limiting, the major species present should be the Rh(I) complex $RhI_2(CO)_2^-$ despite the fact that it is not directly involved in the catalytic cycle! The catalytic cycle is thus entered simply as a drain on the equilibrium represented by the composite of eq 7 and 8.

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Appendix

In the scheme shown in Figure 3, there are six rhodium species, all assumed to be present at constant (steady state) concentrations. The total concentration of rhodium complexes, $[Rh]_t$, is thus the sum of the concentrations of these six species. If steps involving gas evolution are considered irreversible, application of the King–Altman method leads to the following distribution equations:

$$\frac{[\text{Rh(CO)}_2\text{I}_2^-]}{[\text{Rh}]_t} = \frac{k_3k_4k_5k_6(k_{-1}[\text{CO}]^2[\text{H}_2\text{O}] + k_2[\text{CO}]^2[\text{H}_2\text{O}][\text{H}^+][\text{I}^-])}{\Sigma}$$

$$\frac{[\text{HRh(CO)}_2\text{I}_3^-]}{[\text{Rh}]_t} = \frac{k_1k_3k_4k_5k_6[\text{CO}]^2[\text{H}_2\text{O}][\text{H}^+][\text{I}^-]}{\Sigma}$$

$$\frac{[\text{Rh(CO)}_2\text{I}_4^-]}{[\text{Rh}]_t} = \frac{k_1k_2k_3[\text{H}^+]^2[\text{I}^-]^2[\text{CO}](k_5k_6[\text{H}_2\text{O}] + k_{-4}k_6[\text{I}^-] + k_{-5}k_{-4}[\text{H}^+][\text{I}])}{\Sigma}$$

$$\frac{[\text{Rh(CO)I}_5^{2-}]}{[\text{Rh}]_t} = \frac{k_1k_2k_{-3}[\text{H}^+]^2[\text{I}^-]^3(k_5k_6[\text{H}_2\text{O}] + k_{-4}k_6[\text{I}^-] + k_{-5}k_{-4}[\text{H}^+][\text{I}^-])}{\Sigma}$$

$$\frac{[\text{Rh(CO)}_3\text{I}_3]}{[\text{Rh}]_t} = \frac{k_1k_2k_3k_4[\text{H}^+]^2[\text{I}^-]^2[\text{CO}]^2(k_6 + k_{-5}[\text{H}^+])}{\Sigma}$$

$$\frac{[\text{Rh(CO)}_2\text{I}_3(\text{COOH})^-]}{[\text{Rh}]_t} = \frac{k_1k_2k_3k_4k_5[\text{H}^+]^2[\text{I}^-]^2[\text{CO}]^2[\text{H}_2\text{O}]}{\Sigma}$$

where Σ represents the sum of all the terms in the six numerators. The initial rate is then given by

$$\frac{d[H_2]}{dt} = k_2[H^+][I^-][HRh(CO)_2I_3^-]$$

$$= \frac{d[CO_2]}{dt} = k_6[Rh(CO)_2I_3(COOH)^-]$$

$$= \frac{k_1k_2k_3k_4k_5k_6[H^+]^2[I^-]^2[CO]^2[H_2O][Rh]_t}{\Sigma}$$

Since the denominator consists of 12 terms this complete rate equation is rather complex. However, assumptions as to which terms of the denominator are relatively more important lead to considerable simplification, as described in the text.

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(32) Lowering the temperature reversed the color change, and the process was repeatable. The $Rh(CO)_2I_2^-$ complex has very little absorbance above 500 nm, whereas the Rh(III) complexes absorb strongly to above 600 nm. Thus a small amount of Rh(III) gives the solutions a red appearance, while yellow is indicative of almost total Rh(I).

(33) Extrapolation of our data at 70 °C, where the rates of the different limiting reactions are comparable, to 185 °C, assuming activation energies of 30 and 10 kcal/mol for the two regimes, yields temperature enhancement factors of 63 000 and 40, respectively. However, the Monsanto study was conducted at approximately a 50-fold greater CO pressure and one-half the HI concentration. If Rh(III) reduction is first order in P_{CO} and inhibited by $[H^+]$ and $[I^-]$, this gives a further 200-fold enhancement to this regime, whereas, if Rh(I) oxidation depends on $[I^-]^2$ and $[H^+]$, a reduction by $^1/_8$ should be observed. Thus our data predict that the conversion from the conditions of our experiment ($P_{CO} \simeq 0.5$ atm, $[HI] = 2$ M, $T = 70$ °C) to the conditions of Singleton et al. ($P_{CO} \simeq 25$ atm, $[HI] \simeq 1$ M, $T = 185$ °C) should increase the rates of both the oxidation and reduction reactions by a comparable amount, as seen below:

Rate Enhancement Factors

	temp increase	P_{CO}	[HI]	total
Rh^{III} reduction	40×	50×	4×	8000×
Rh^{I} oxidation	6300×	1×	$^1/_8$×	7875×

The key point of this back-of-the-envelope analysis is that, although quite different conditions were employed, both studies lead to the observation of the two different kinetic regimes through relatively small concentration variations.

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$$HRh(CO)_2I_3^- \underset{(k_{1a})\ CO}{\overset{(k_{2a})\ I^-}{\rightleftarrows}} HRh(CO)I_4^{2-} \xrightarrow[H^+]{(k_{2b})} Rh(CO)I_4^- + H_2$$

with the first proceeding by an I_a mechanism, the following possibilities emerge if 2a is taken as rate limiting: (i) if $k_{2b}[H^+] \gg k_{-2a}[CO]$ then the rate is CO independent; (ii) if $k_{2b}[H^+] \ll k_{-2a}[CO]$, then the rate will show CO inhibition. Hence under the different conditions of 400 Torr and 400 psig of the two studies, (i) and (ii) are being followed, respectively.

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(45) The intimate mechanism of steps 1 and 2 cannot be determined and may, in fact, change with conditions, leading to the difference in CO dependence between the present study and that of Singleton et al.

(46) Slow CO_2 elimination from hydroxycarbonyls relative to the back-reaction, k_{-5}, has precedent. See D. J. Darensbourg and J. A. Froelich, *J. Am. Chem. Soc.*, **99**, 4726 (1977), and references cited therein.