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Homogeneous WGS Reaction Promoted by Rhodium Carbonyls in Aqueous Pyridine: An Acid-Cocatalyzed Reaction Which Proceeds to the Complete Consumption of Water and Is Inhibited by Chloride Ions

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Homogeneous WGS catalysis employing $Rh_4(CO)_{12}$ as precursor in aqueous pyridine (py) was investigated in a batch reactor at 80 °C, P_{CO} = 1 atm, and [Rh] = 0.02 M. The WGSR has the highest activity in py containing 3% H_2O, and can be protracted to the complete consumption of water. $[L_xH][Rh_5(CO)_{13}(py)_2]$ (L = H_2O, py) was found to accumulate during the catalysis, while protracted WGSR leaves $[Rh(CO)_n(py)_{4-n}][Rh_5(CO)_{13}(py)_2]$ (n = 1, 2) in dehydrated py. Separate experiments confirmed that in anhydrous py at 80 °C $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ gives H_2 and $[Rh(CO)_n(py)_{4-n}][Rh_5(CO)_{13}(py)_2]$, while in wet py at 30 °C the latter rhodium species is reduced by CO back to $[L_xH][Rh_5(CO)_{13}(py)_2]$, with CO_2 formation. Hence, a catalytic cycle is proposed where *cis*-$[Rh(CO)_2(py)_2]^+$ and $[Rh_5(CO)_{13}(py)_2]^-$ are the active species, and where H_2 and CO_2 production accompanies their mutual interconversion. Direct investigation of the catalytic reaction showed an inhibiting effect by chloride ions at <5% H_2O. The reaction resulted to be acid cocatalyzed up to a limiting behavior. Both these aspects are explained on the basis of the chemical properties of the two proposed active species, which were elucidated by separate experiments. While a systematic study was not attempted, a TOF(H_2) = 172 (T = 80 °C, P_{CO} = 1 atm, [Rh] = 0.02 M) was achieved in py containing 3% H_2O when a chloride-free precursor is employed in the presence of added acid (CF_3SO_3H/Rh = 10).

Introduction

Commercially, WGSR produces H_2 and CO_2 from gaseous H_2O and CO over solid metal oxide catalysts at high temperatures.[1] The possibility of homogeneous WGSR, which requires a lower thermal input and employes liquid H_2O, was independently demonstrated by three research groups.[2] Since their seminal work, numerous catalytic systems for homogeneous WGSR were studied and the fundamental reaction mechanism was elucidated.[3] Mandatory intermediates are metallacarboxylic acids derived from attack of water or hydroxide ions onto electron-deficient carbonyls.[4] This applies also to the Rh/aqueous amine system, one of the most active in promoting homogeneous WGSR, where the intervention of cationic carbonyl complexes has been envisaged. The CO stretching IR absorptions of an active aqueous 4-picoline or py solution where $RhCl_3$ had been employed as a precursor (ν_{CO} = 2040 s, 2010 s, 1980 vs, 1820 s and 1760 s cm^{-1}) were tentatively attributed to polynuclear cationic rhodium complexes.[5]

However, in the light of our recent work,[6] the IR spectrum must be attributed to the anionic cluster $[Rh_5(CO)_{13}(py)_2]^-$, the species accumulating during the catalysis. On the other hand, since its CO ligands do not undergo nucleophilic attack by water, it is apparent that more labile intermediates work for the Rh-promoted homogeneous WGSR. Their nature and the role of $[Rh_5(CO)_{13}(py)_2]^-$ are elucidated in this paper.

Experimental Section

General Methods. Unless otherwise specified, all operations were carried out under argon by standard Schlenk techniques. CO (<0.1% H_2) was purchased from Matheson and dried by passage over activated molecular sieves. Anhydrous py was obtained by refluxing during 36 h the AR grade solvent over finely ground CaH_2 and then distilling it under an Ar atmosphere. AR grade Et_2O was distilled under an Ar atmosphere from $LiAlH_4$. Rhodium trichloride hydrate (40–42% Rh) was used as received from Chimet SpA. The 40% aqueous solution of $[Na(n\text{-}Bu)_4]OH$ was purchased from Fluka. The rhodium complexes $Rh_4(CO)_{12}$[7] and *cis*-$[Rh(CO)_2(py)_2][BPh_4]$[8] were prepared by literature methods. The IR spectra were recorded on a Perkin-Elmer Model FT-IR 1725-X instrument. Liquid samples for infrared spectra were taken off with a syringe and transferred to a 0.1 mm CaF_2 cell. Quantitative determination of H_2O in diluted py solution (H_2O concentration < 1%) were performed by comparing the absorbance of the 3412-cm^{-1} band with a calibration curve. Analysis of gas samples from catalysis runs were performed by a DANI Model 3200 gas chromatograph equipped with HW detector and a molecular sieve column, with Ar as carrier gas. Calibration curves were prepared periodically for CO and H_2.

Batch Reactor Procedures. Catalytic activity runs were carried out in an all-glass vessel similar to that described in ref 3a with a volume of 341 mL. During a typical run, gas samples (1 mL) were removed at 15-min intervals and analyzed by GC.

Preparation of $[(py)_2H][Rh_5(CO)_{13}(py)_2]$.[6] $Rh_4(CO)_{12}$ (12.76 g, 17.06 mmol) was dissolved in py (160 ml) containing 0.3 mL of H_2O. The solution was stirred under CO for 4 h at room temperature. Et_2O (900 mL) was then added; after 4 h at 2 °C, $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ (14 g, 86%) was collected by filtration as red crystals analyzing satisfactorily.

Synthesis of $[N(n\text{-}Bu)_4][Rh_5(CO)_{13}(py)_2]$. $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ (8.37 g, 7.0 mmol) was dissolved in 70 mL of py, and 4.7 g of a 40% aqueous solution of $[N(n\text{-}Bu)_4]OH$ were added under a CO atmosphere. The addition of 200 mL of H_2O brought about the formation of a dark oil, which gradually solidified, giving a brick red solid, which was collected by filtration, washed with 40 ml of H_2O, and dried under vacuum (0.1 Torr). Thus 7.5 g (84%) of $N(n\text{-}Bu)_4][Rh_5(CO)_{13}(py)_2]$ was obtained and gave satisfactory analytical data. FT-IR (py, CO atmosphere): ν_{CO} 2040 s, 2010 s, 1980 vs, 1820 s, and 1760 s cm^{-1}.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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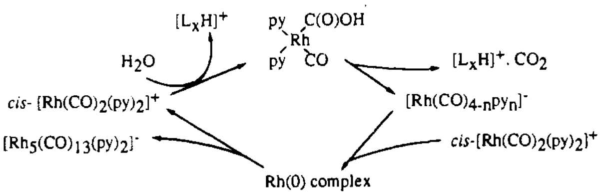
Scheme 1. Proposed Mechanism for the Formation of $\mathrm{CO_2}$ and $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (L = $\mathrm{H_2O}$, py) from *cis*-$[\mathrm{Rh(CO)_2(py)_2}]^+$ and $\mathrm{CO/H_2O}$ in py



Results and Discussion

$\mathrm{CO_2}$ and $\mathrm{H_2}$ from the Reactions Interconverting $[\mathrm{Rh(CO)}_n\mathrm{(py)}_{4-n}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (n = 1, 4) and $(\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (L = py, $\mathrm{H_2O}$). We showed recently[6] that $\mathrm{Rh_4(CO)_{12}}$ disproportionates immediately and irreversibly in anhydrous py, the anionic cluster $[\mathrm{Rh_5(CO)_{13}(py)_2}]^-$ and the mononuclear cationic complex $[\mathrm{Rh(CO)(py)_3}]^+$ being formed under an argon atmosphere (eq 1).

$$^{3}/_{2}\mathrm{Rh_4(CO)_{12}} \xrightarrow{\mathrm{py,\ Ar}} [\mathrm{Rh_5(CO)_{13}(py)_2}]^- + [\mathrm{Rh(CO)(py)_3}]^+ + 4\mathrm{CO} \tag{1}$$

Under a CO atmosphere (P_{CO} = 735 Torr), equilibrium 2 was observed[6] and a $[\mathrm{Rh(CO)(py)_3}]^+/cis\text{-}[\mathrm{Rh(CO)_2(py)_2}]^+ = 1.55$ molar ratio was determined at 30 °C.

$$[\mathrm{Rh(CO)(py)_3}]^+ + \mathrm{CO} \rightleftarrows cis\text{-}[\mathrm{Rh(CO)_2(py)_2}]^+ + \mathrm{py} \tag{2}$$

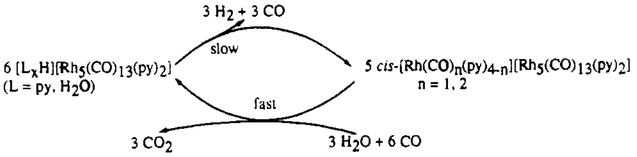
When the ionic products of the disproportionation of $\mathrm{Rh_4(CO)_{12}}$ in py (eq 1) were reacted with $\mathrm{H_2O}$ under a CO atmosphere, the equilibrium mixture of the cations was quantitatively reduced to $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (L = py, $\mathrm{H_2O}$) with $\mathrm{CO_2}$ formation (eq 3).[6]

$$\underset{n = 1, 2}{5[\mathrm{Rh(CO)}_n\mathrm{(py)}_{4-n}][\mathrm{Rh_5(CO)_{13}(py)_2}]} \xrightarrow{\mathrm{py,\ CO/H_2O,\ 30\ ^\circ C}} \underset{\mathrm{L = H_2O,\ py}}{3\mathrm{CO_2} + 6[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]} \tag{3}$$

Separate experiments showed that an equilibrium mixture of the two cations reacts with $\mathrm{CO/H_2O}$ even in very diluted py solutions of $\mathrm{H_2O}$. Under a P_{CO} = 1 atm, the addition of 0.5% $\mathrm{H_2O}$ to a yellow 0.1 M py solution of *cis*-$[\mathrm{Rh(CO)_2(py)_2}][\mathrm{BPh_4}]$ brought about gas absorption, while the color turned red. The reaction was monitored by IR spectroscopy: after 2 h at room temperature, the cationic carbonyls were quantitatively transformed into $[\mathrm{Rh_5(CO)_{13}(py)_2}]^-$ (eq 3). No reaction with $\mathrm{H_2O}$ was observed under Ar. On substituting CO with an inert atmosphere, *cis*-$[\mathrm{Rh(CO)_2(py)_2}]^+$ is wholly converted into $[\mathrm{Rh(CO)(py)_3}]^+$, and only the CO groups of the dicarbonyl complex undergo nucleophilic attack by water.

The proton elimination in aqueous py encompasses the decarboxylation of the probable metallacarboxylic acid intermediate (Scheme 1). Neither dihydrogen is evolved nor hydrido complexes accumulate; therefore, the formation of an anionic mononuclear carbonyl complex is to be envisaged. This latter would then annihilate its charge with that of an unreacted *cis*-$[\mathrm{Rh(CO)_2(py)_2}]^+$. Like $\mathrm{Rh_4(CO)_{12}}$ (eq 1), the so formed Rh(O) complex is expected to disproportionate; thus, the cyclic reaction of Scheme 1 results in $\mathrm{CO_2}$ formation and in $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ accumulation.

Scheme 2. Proposed Mechanism for the Rh-Promoted WGSR in Aqueous Amines



Reaction 3 can constitute the $\mathrm{CO_2}$-producing step of the rhodium-promoted homogeneous WGSR. In fact, the catalytic cycle can be completed with the thermal decomposition of $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (L = $\mathrm{H_2O}$, py) at 80 °C (*i.e.*, the temperature required for catalytic WGS). The quantitative reduction of the proton to $\mathrm{H_2}$ was observed in a 0.02 M solution of $[\mathrm{(py)_2H}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ in anhydrous py. $[\mathrm{Rh_5(CO)_{13}(py)_2}]^-$ behaves as a 6-e-reducing agent and the formation of the cationic mononuclear Rh(I) carbonyls accompanies the reaction (eq 4).

$$6[\mathrm{(py)_2H}][\mathrm{Rh_5(CO)_{13}(py)_2}] \xrightarrow[-\mathrm{CO}]{\mathrm{py,\ 80\ ^\circ C}} 3\mathrm{H_2} + 5[\mathrm{Rh(CO)_2(py)_2}][\mathrm{Rh_5(CO)_{13}(py)_2}] \tag{4}$$

When combined, reactions 3 and 4 result in WGSR and can constitute the two steps of the catalytic process, where $\mathrm{H_2}$ production constitutes the slow step.

Kinetic investigations by Ford with $\mathrm{RhCl_3}$ as precursor[5] agree with the intervention of a polynuclear intermediate during the slow step of catalytic WGS. The direct observation of the two active species during the catalytic WGS is reported below and further supports the mechanism of Scheme 2.

Detection of $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ and of $[\mathrm{Rh(CO)}_n\mathrm{(py)}_{4-n}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (n = 1, 4) during the Catalytic WGS. We investigated the catalytic reaction by employing the chloride free precursor $\mathrm{Rh_4(CO)_{12}}$. According to the eq 1 and eq 3 reaction sequence, $[\mathrm{Rh_5(CO)_{13}(py)_2}]^-$, with a proton in various environments as its countercation, turned out to be the only species containing Rh in a solution prepared by dissolving $\mathrm{Rh_4(CO)_{12}}$ ([Rh] = 0.02 M) in py containing 3% water, under P_{CO} = 1 atm. When the temperature of this solution was raised to 80 °C at constant P_{CO}, we observed catalytic production of $\mathrm{CO_2}$ and $\mathrm{H_2}$, without any induction period. The IR spectrum of a hot sample, taken during the WGSR when 10 mol of $\mathrm{H_2O}$ *per* Rh had reacted, displayed absorptions due to $[\mathrm{Rh_5(CO)_{13}(py)_2}]^-$ (ν_{CO} = 2040 m, 2011 m, 1980 vs, 1818 m and 1756 m $\mathrm{cm^{-1}}$), thus directly confirming that $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$ (L = $\mathrm{H_2O}$, py) is the species which accumulates during the catalytic process.[9]

Remarkably, the catalysis can be protracted to the complete consumption of water. At <0.1% $\mathrm{H_2O}$, the IR spectrum of the solution showed three bands, indicative of a P_{CO}-dependent equilibrium mixture of *cis*-$[\mathrm{Rh(CO)_2(py)(_2}]^+$ (ν_{CO} = 2100 and 2038 $\mathrm{cm^{-1}}$) and $[\mathrm{Rh(CO)(py)_3}]^+$ (ν_{CO} = 1993 $\mathrm{cm^{-1}}$) (eq 2), thus showing that, during the catalysis, the labile mononuclear cationic intermediates can also be directly detected, but only at very low water concentrations.

Such an extreme WGSR which continues to the complete consumption of water is unprecedented, and so it was investigated more in detail. Our study showed two hitherto unrecognized aspects of the WGSR promoted by rhodium carbonyls in aqueous amines; namely, the inhibiting effect of chloride ions at low $\mathrm{H_2O}$ concentration and the cocatalytic effect of acids. These two effects can be invoked in favor of the mechanism outlined in Scheme 2, since they can well be rationalized on the basis of the properties of the two proposed active species, *i.e.* *cis*-$[\mathrm{Rh(CO)_2(py)_2}]^+$ and $[\mathrm{L_xH}][\mathrm{Rh_5(CO)_{13}(py)_2}]$.

Inhibiting Effect of Chloride Ions on WGSR in py Containing $\mathrm{H_2O}$ < 5%. When $\mathrm{Rh_4(CO)_{12}}$ was the precursor, the WGSR activity in py reached a maximum at 3% $\mathrm{H_2O}$. However, TOF($\mathrm{H_2}$) = 42 (mol/mol of Rh)/day at 80 °C, and [Rh] = 0.02 M

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[9] At higher rhodium concentrations, IR absorptions due to clusters of higher nuclearity can also be observed.

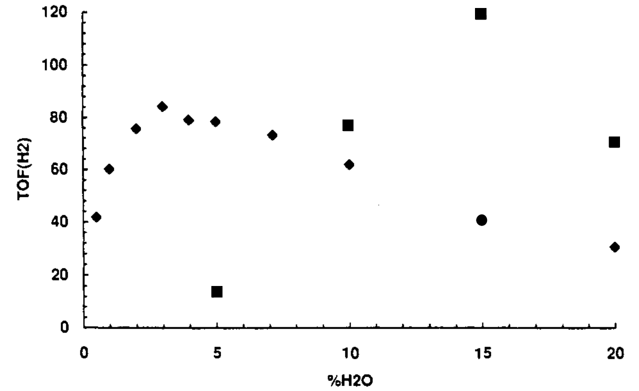

Figure 1. Turnover frequency ((mol/mol of Rh)/day) for H_2 production *vs* % H_2O in py for WGS catalysis at 80 °C under P_{CO} = 1 atm by a 0.02 M rhodium solution prepared from $RhCl_3$ (■) and from $Rh_4(CO)_{12}$ (◆).

was still observed at 0.5% H_2O. For comparison, when $RhCl_3$ was employed instead as precursor, the catalytic rate under the same conditions was a maximum at 15% H_2O (TOF(H_2) = 120) while WGSR nearly stops at <5% H_2O (Figure 1). The inhibiting effect of chloride ions at <5% H_2O is apparent and is to be attributed to the formation of Rh(I) chloro carbonyl complexes which are both stable and inert. These can be detected directly in the IR spectrum of solutions showing very little activity as a consequence of both the presence of chloride ions and low H_2O concentration. As shown before, when $Rh_4(CO)_{12}$ was employed as precursor in py containig 2% H_2O ([Rh] = 0.02 M), $[L_xH][Rh_5(CO)_{13}(py)_2]$ was the species which accumulated during the catalytic WGS. When the reaction was frozen by addition of PPNCl (Cl/Rh = 2), the IR spectrum of the solution showed absorptions at 2084 and 2063 cm^{-1}, diagnostic[10] for the neutral *cis*-$[RhCl(CO)_2(py)]$ and the anionic *cis*-$[RhCl_2(CO)_2]^-$, which accompany the bands of $[Rh_5(CO)_{13}(py)_2]^-$. The higher stability of the chlorocarbonyl complexes with respect to *cis*-$[Rh(CO)_2(py)_2]^+$ and their inertness to nucleophilic attack by H_2O were separately proved. As already established,[6] the IR spectrum of a 0.1 M py solution of *cis*-$[Rh(CO)_2(py)_2][BPh_4]$, at 30 °C and under a CO atmosphere, pertains to an equilibrium mixture of $[Rh(CO)(py)_3]^+$ (ν_{CO} = 1993 cm^{-1}) and of *cis*-$[Rh(CO)_2(py)_2]^+$ (ν_{CO} = 2100 and 2038 cm^{-1}) (eq 2). Upon addition of PPNCl (Cl/Rh = 1) to this solution maintained under a CO atmosphere, only the absorptions of *cis*-$[RhCl(CO)_2(py)]$ (ν_{CO} = 2084 and 2009 cm^{-1}) could be detected. A synergistic effect of chloride ions and CO in stabilizing the dicarbonylchloro-complex is apparent (eq 5).

$$\left\{\begin{array}{c} cis\text{-}[Rh(CO)_2(py)_2]^+ \\ CO \Big\Updownarrow \text{-}CO \\ [Rh(CO)(py)_3]^+ \end{array}\right\} + Cl^- \xrightarrow{CO} cis\text{-}[RhCl(CO)_2(py)] \qquad (5)$$

At the higher Cl/Rh = 3 molar ratio, the bands of the anionic *cis*-$[RhCl_2(CO)_2]^-$ (ν_{CO} = 2063 and 1984 cm^{-1}) can also be detected. As far as the inertness of chloro carbonyl complexes is concerned, on comparing their CO stretching frequencies with those of *cis*-$[Rh(CO)_2(py)_2]^+$, it appears that the incoming Cl^- ligands increase the electron density of the CO groups and therefore prevent nucleophilic attack by water. The inhibiting effect of chloride ions is due to formation of chloro carbonyl Rh(I) complexes, as confirmed when the sensitivity of the WGSR activity to the Cl/Rh ratio was probed by examining the ratios 3, 2, 1, 0.5, 0.2, and 0.1 at constant H_2O concentration (2%). It can be seen from Figure 2 that the inhibiting effect of Cl^- goes on down to high Cl^- dilution: with a Cl/Rh ratio of 0.2 the TOF(H_2) is still 10 times slower than that in the absence of chloride. Only at a Cl/Rh molar ratio < 1/6 does the poisoning effect of chlorides begin to diminish. This can be understood if one remembers that, at a Cl/Rh molar ratio of 1/6, the chloride is still sufficient to convert the labile intermediate *cis*-$[Rh(CO)_2(py)_2]^+$ quantitatively into the inert *cis*-$[RhCl(CO)_2(py)]$, since the concentration of Rh(I) species cannot exceed one-sixth of the total Rh concentration (Scheme 2).

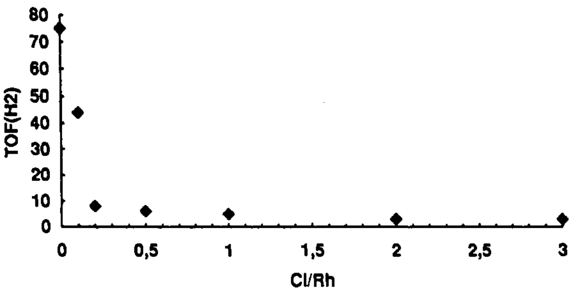

Figure 2. Plot of TOF(H_2) *vs* PPNCl/Rh molar ratio. Data were obtained in py containing 2% H_2O, at *T* = 80 °C, P_{CO} = 1 atm, and [Rh] = 0.02 M, introduced as $Rh_4(CO)_{12}$.

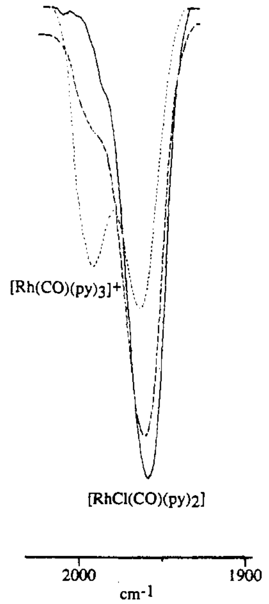

Figure 3. IR spectra in the CO stretching region of 0.06 M solutions of $RhCl(CO)(py_3)$ in py containing increasing H_2O concentrations. The IR absorption of the py/H_2O medium have been subtracted. Key: (—) anhydrous py; (- -) 7% H_2O; (···) 15% H_2O.

It remains to explain why the quenching effect of Cl^- vanishes if the concentration of H_2O is >5%. The effect of increasing water concentration has been enucleated in aqueous py solutions of $[RhCl(CO)(py)_3]$ kept under an inert atmosphere. As already mentioned, $[Rh(CO)(py)_3]^+$ is formed quantitatively in a 0.06 M py solution of *cis*-$[Rh(CO)_2(py)_2][BPh_4]$ on substituting CO with an Ar atmosphere. Upon addition of 3 equiv of PPNCl, the 1993-cm^{-1} band of the latter is shifted to 1957 cm^{-1} as a consequence of the substitution of a py molecule by a chloro ligand in the Rh coordination sphere. When water concentration is increased, the 1957-cm^{-1} band of the chloro carbonyl complex remains the only CO stretching absorption detectable in py till H_2O reaches 5%. At higher H_2O concentrations, however, the 1993-cm^{-1} band of the ionic $[Rh(CO)(py)_3]^+$ grows in (Figure 3).

The most obvious explanation for such a behavior requires us to consider that substantial amounts of H_2O increase the dielectric constant of the medium, thus favoring the formation of ionic species, *i.e.* the release of Cl^- from the coordination sphere of the Rh(I) complex. From the point of view of the catalytic reaction, it can be assumed by analogy that the quenching effect of Cl^-

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[10] Lawson, D. N.; Wilkinson, G. *J. Chem. Soc.* **1965**, 1900.

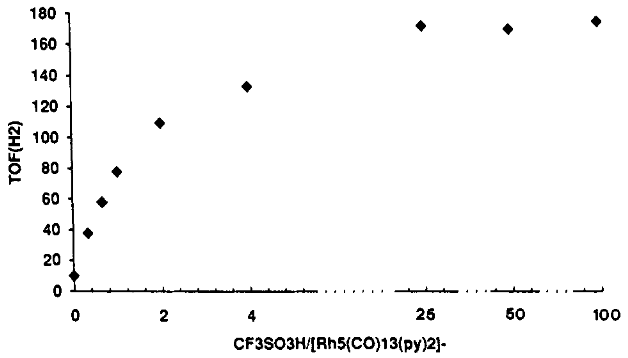

Figure 4. Plot of TOF(H_2) *vs.* $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ molar ratio. Data were obtained in py containing 3% H_2O, at T = 80 °C, P_{CO} = 1 atm, and [Rh] = 0.02 M.

vanishes at high H_2O concentration, since the inert Rh(I) chloro carbonyl complexes are in equilibrium with the labile *cis*-$[Rh(CO)_2(py)_2]^+$ intermediate in the medium of increased dielectric constant.

The Acid Cocatalysis. In the course of our investigation of the inhibiting effect of chloride ions we found that, at the same H_2O concentration (15%), the WGSR rates with $RhCl_3$ and $Rh_4(CO)_{12}$ as precursors differ, even when (PPN)Cl is added to the latter in a Cl/Rh = 3 molar ratio. In the first case, TOF(H_2) = 120 (Figure 1) is doubled, although the parameters currently considered to affect the WGSR (T = 80 °C, P_{CO} = 1 atm, [Rh] = 0.02 M, 15% H_2O, Cl/Rh = 3 (molar ratio)) have the same values. Looking for the neglected parameter, we considered that in the case of $RhCl_3$ there is an induction period before the "mature" solution of $[Rh_5(CO)_{13}(py)_2]^-$ is obtained. This time is required for reaction 6 which produces, *inter alia*, protons in various environments.

$$5RhCl_3 + 8H_2O + 21CO \xrightarrow{py} [Rh_5(CO)_{13}(py)_2]^- + \underset{L = py,\ H_2O}{16[L_xH]^+} + 8CO_2 + 15Cl^- \quad (6)$$

It appears therefore that, at the same Rh and Cl^- concentrations, the catalysis with $RhCl_3$ as precursor proceeds with a steady state concentration of acid which is 16 times higher than that with $PPNCl/Rh_4(CO)_{12}$. In fact, when this latter precursor is employed, the active species $[Rh_5(CO)_{13}(py)_2]^-$ is generated together with only 1 equiv of protons, as a consequence of the eq 1 and eq 3 reaction sequence. On the other hand, since the reduction of the proton by the anionic cluster constitutes the slow step of the Rh-promoted WGSR (Scheme 2), an acid is expected to enhance the catalysis rate; hence, it is not surprising that the $RhCl_3$ precursor could result more efficient than $Rh_4(CO)_{12}$ when a high H_2O concentration attenuates the Cl^- inhibiting effect.

In order to free our investigation from any additional effect due to the use of a precursor, the cocatalysis by acid was studied by employing directly the $[Rh_5(CO)_{13}(py)_2]^-$ active species as its tetrabutylammonium salt. The sensitivity of WGSR activity to the acid/Rh ratio was probed in py containing 3% H_2O with $[N(n\text{-}Bu)_4][Rh_5(CO)_{13}(py)_2]$ = 0.004 M, P_{CO} = 1 atm, and T = 80 °C, and the $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ = 0, 0.33, 0.66, 1, 2, 4, 25, 50, 100 molar ratios were examined. It can be seen from Figure 4 that, in the absence of acid, $[Rh_5(CO)_{13}(py)_2]^-$ is scarcely active for WGSR, while there is a sharp increase of TOF(H_2) as soon as acid is added. This behavior agrees with the basic mechanism of Scheme 2, where the slow step of WGSR is envisaged as the reduction of the proton by the anionic cluster: a nearly linear dependence between $[CF_3SO_3H]$ and TOF(H_2) is found, up to $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ = 5. At higher $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ molar ratios, a limiting behavior is observed: a new rate-limiting step turns up at the higher rates allowed by the acid cocatalyst. When $Rh_4(CO)_{12}$ is employed as precursor, in agreement with the statement that this precursor is converted into $[L_xH][Rh_5(CO)_{13}(py)_2]$, the TOF($H_2$) under comparable conditions resulted in absence of added acid to be 84; within the experimental error, this value is the same of that found when $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ = 1 (TOF(H_2) = 78). The nature of the species which then accumulate and that of the intermediates for the electron transfer from $[Rh_5(CO)_{13}(py)_2]^-$ to the proton (eq 4) will be elucidated in a forthcoming paper.

Finally, the TOF(H_2) = 172, determined in py containing 3% H_2O, [Rh] = 0.02 M, $CF_3SO_3H/[Rh_5(CO)_{13}(py)_2]^-$ = 25, P_{CO} = 1 atm, and T = 80 °C (Figure 4), can be compared with TOF(H_2) = 120, which is the highest value obtained under the same conditions at 15% H_2O by employing $RhCl_3$ as precursor (Figure 1). A substantial improvement in the efficiency of the Rh/aqueous amine system results when an acid cocatayst is employed in a halide free solution at low H_2O concentration.

Conclusions. The presently investigated WGSR promoted by the Rh/aq. amine system constitutes a lucky case, since it offered (*i*) the opportunity to detect the active species directly, (*ii*) numerous confirmations of their intervention, and (*iii*) an improvement of the catalytic efficiency. A strict relationship between the relevant aspects of the reaction and the chemistry of the proposed active species, namely *cis*-$[Rh(CO)_2(py)_2]^+$ and $[Rh_5(CO)_{13}(py)_2]^-$, has been established. Chloride ions inhibit catalysis at low H_2O concentrations, and Rh(I) chloro carbonyl complexes can be detected in solutions which show very little activity. Correspondingly, it was found that *cis*-$[Rh(CO)_2(py)_2]^+$ is converted by chlorides into the same stable Rh(I) chloro carbonyl complexes which are inert toward nucleophilic attack by water. At H_2O concentration >5%, the inhibiting effect of chlorides vanishes, because the Rh(I) chloro carbonyl complexes dissociate chloride ions and restore the labile *cis*-$[Rh(CO)_2(py)_2]^+$. At 2% H_2O the inhibiting effect of chloride ions holds on down to Cl/Rh = 1/6; at this stoicheiometric ratio the *cis*-$[Rh(CO)_2(py)_2]^+$ labile intermediate cannot form, because five-sixths of the total Rh is present as the anionic cluster $[Rh_5(CO)_{13}(py)_2]^-$ (Scheme 2), while the remaining one-sixth of the Rh is highly stable as $[RhCl(CO)_2(py)]$. Finally, the observed cocatalytic effect of added acids agrees with the mechanism of Scheme 2, where the slow step of the catalytic reaction is represented by the reduction of the proton in various environments (py, H_2O).

These findings disclose a so far never considered mechanism for catalytic WGS: both mononuclear cationic and polynuclear anionic carbonyls are active species. The cation *cis*-$[Rh(CO)_2(py)_2]^+$ activates CO toward nucleophilic attack by water, CO_2 and $[L_xH][Rh_5(CO)_{13}(py)_2]$ being formed. On the other hand, $[Rh_5(CO)_{13}(py)_2]^-$ acts as an electron reservoir for the reduction of the proton; only at higher temperatures does an electron transfer which results in the formation of H_2 and restoration of *cis*-$[Rh(CO)_2(py)_2]^+$ occur. The interconversion of the two active ionic species has been assumed to proceed through neutral rhodium carbonyls and their disproportionation in amines (eq 1). A relationship between the disproportionation reaction of metal carbonyls and WGSR is thus sketched out.

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