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HOMOGENEOUS CATALYSIS OF THE WATER–GAS SHIFT REACTION BY RUTHENIUM CARBONYL COMPLEXES: STUDIES IN ACIDIC SOLUTIONS

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Summary

Homogeneous catalysis of the water–gas shift reaction has been demonstrated for a system based upon $Ru_3(CO)_{12}$ in aqueous acidic diglyme solutions. At low partial pressures of carbon monoxide ($P_{CO} < 1$ atm) the catalysis rate shows a first-order dependence upon both P_{CO} and the total ruthenium concentration. *In situ* spectroscopic studies on the working catalyst lead to the formulation of the principal ruthenium species as a cationic dinuclear ruthenium carbonyl hydride derivative. The catalyst system shows a marked decrease in activity when P_{CO} exceeds 1 atm, and this is attributed to an equilibrium between the dinuclear ruthenium hydride and $Ru_3(CO)_{12}$ favouring the latter at high values of P_{CO}. A cyclic mechanism is proposed for the shift reaction catalysis and the system's activity dependence on various solution parameters.

Introduction

The past several years have witnessed a resurgence of interest in the catalysis of the water–gas shift reaction (WGSR) (eqn. 1) stimulated by the discovery of homogeneous catalyst systems based upon definable metal complexes [1 - 6].

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

This interest stems primarily from the importance of the WGSR to schemes for the production of gaseous and liquid fuels and other organic products from coal, and also from the associated reactions of carbon monoxide and water such as the Reppe modification of the hydroformylation reaction.

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Earlier reports from this laboratory described a WGSR catalyst based upon ruthenium carbonyl in aqueous alkaline 2-ethoxyethanol solutions [1, 7]. A primary reason for the choice of this reaction medium was the consideration that the key step is CO activation by nucleophilic attack. Thus one can postulate a mechanism by which coordinated carbon monoxide, L_xMCO, undergoes attack by hydroxide to give a hydroxycarbonyl species $[L_xMOCO_2H]^-$ which decarboxylates to give a metal hydride anion (eqn. 2).

$$L_xMCO + OH^- \rightleftharpoons [L_xMCO_2H]^- \longrightarrow [L_xMH]^- + CO_2 \quad (2)$$

Subsequent protonation of this complex would afford the hydride L_xMH_2 from which elimination of dihydrogen might occur (alternatively, dihydrogen elimination might be assisted by the attack of CO on the $[L_xMH]^-$ or $[L_xMH_2]$ complexes). Such a postulated mechanism appears to be followed for the alkaline ruthenium carbonyl system, with the additional feature that the rate-limiting process is dihydrogen elimination [7].

In acidic solution one can envision a similar mechanism in which the CO activation step is attack by H_2O on the carbonyl. Under such conditions, CO activation may possibly be assisted by protonation of the metal center (*e.g.* eqn. 3) or of the carbonyl oxygen.

$$L_xMCO + H^+ \rightleftharpoons [HL_xMCO]^+ \quad (3)$$

Furthermore, a dihydrogen elimination step requiring L_xMH_2 formation would be more favourable in an acidic environment.

That acidic solutions should be a viable medium for the WGSR catalysis was first demonstrated by Cheng *et al.* for a rhodium catalyst in aqueous acetic acid [2] and subsequently by this laboratory for a system based upon ruthenium carbonyl in acidic aqueous diglyme [8]. We report here studies aimed at providing a more complete description of the latter catalysis system. These studies include *in situ* spectral investigations of working catalysts at elevated temperatures (100 °C) and various CO pressures up to 2.5 atm.

Notably, the chemistry of acidic ruthenium carbonyl systems has drawn attention in other areas of catalysis. Two recent reports from industrial laboratories show that such systems, under conditions of high temperature and pressure, are active catalysts for the production of ethylene glycol derivatives from synthesis gas [9], and for the synthesis gas homologation of esters and carboxylic acids [10].

Experimental

Reagents

2-Ethoxyethanol (Mallinckrodt) was distilled from anhydrous stannous chloride followed by distillation from magnesium turnings. Diglyme (Mallinckrodt) was distilled from calcium hydride, tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled from sodium benzophenone ketyl and methanol was distilled from magnesium methoxide. Sulphuric acid

(Mallinckrodt) was diluted with water to *ca.* 5 M, and its concentration determined by titration. Acetic, trifluoroacetic and phosphoric acids (Mallinckrodt) were used as received, the appropriate amount being delivered by microliter syringe. Carbon monoxide/methane, 94%/6%, hydrogen and argon, all prepurified grade, were obtained from Linde. $Ru_3(CO)_{12}$ [11], $Ru_3(CO)_9(PPh_3)_3$ [12], and $H_4Ru_4(CO)_{12}$ [13] were prepared by the reported procedures; $Fe(CO)_5$ was obtained from Alfa Inorganics.

Apparatus

Gas sample analyses were performed using a Hewlett Packard 5830A programmable gas chromatograph with Carbosieve B 80-100 mesh columns obtained from Hewlett Packard; the carrier gas was 8%/92% hydrogen/helium mixture obtained from Linde. Gas samples were taken with Analytical Pressure Lok syringes obtained from Pressure Sampling Corporation. Calibration curves were recorded at periodic intervals for H_2, CO and CO_2, and were found to be linear for the latter two gases but not for H_2. Proton and ^{13}C NMR spectra were recorded on Varian Associates CFT 20 or XL100 spectrometers, or a Nicolet NCT300 spectrometer operating in the F.T. mode and equipped with temperature controllers accurate to ±2 °C. The spectra were recorded in diglyme d-14 (Merck, Sharpe and Dohme) at 100 °C under an atmosphere of CO. Infrared spectra were recorded on a Perkin Elmer 683 IR spectrometer. The IR spectra of acid/aqueous diglyme catalytic solutions at room temperature were recorded between Irtran-2 plates separated by 2 mm stainless steel spacers with a 14% hexane/diglyme solution as a reference. IR spectra of catalytic solutions recorded at 100 °C under 0.9 atm of CO were recorded in a cell similar to that described by King [14]. UV spectra were recorded on a Cary 118C spectrophotometer.

Catalytic runs and product analysis

Catalytic runs were carried out in all-glass reactors with one of two stopcocks attached to the vacuum line and the other fitted with a serum cap to permit periodic sampling of the gas phase. In a typical run, $Ru_3(CO)_{12}$ (0.054 mmol) was placed in a glass reaction vessel and a 5 ml portion of the solvent, either 2-ethoxyethanol or diglyme, each 8.0 M in water and 0.25 M in sulphuric acid, was added. The reaction vessel was attached to the vacuum line, which possessed an attached manometer and relevant gas inlets. The solution was degassed by two freeze–thaw–pump cycles using liquid nitrogen as the coolant. The reaction vessel was then charged with CO/CH_4 0.76 atm (0.9 atm at 100 °C) and suspended in an oil bath thermostatted at 100 °C.

Samples were withdrawn from the reaction vessel via the serum cap at bath temperature, or by expansion of the gas phase into a small portion of the vacuum line whence the gas was sampled via a septum. The latter method was used for sampling during the induction period when the flask was recharged after each sample had been withdrawn, (usually at hourly intervals); the former method was used for the recording of kinetic data. Care was taken to record data points used for the calculation of daily turnover frequencies at low CO consumption, $<15\%$.

The reaction stoichiometries were analyzed using methane as the internal calibrant. The CO/CH_4 ratio of the unreacted gas mixture, coupled with the known quantity of the initial amount of CO and the gas phase component percentages, allowed for the calculation of the absolute amount of H_2 and CO_2 produced and the amount of CO consumed. The amount of H_2 was corrected for a small background count.

The induction period was examined by measuring the activity of a solution every hour. After each sampling, the solution was subjected to a freeze–pump–thaw cycle and recharged with CO. The induction period was also examined for WGSR mixtures matured under either H_2 or N_2.

For the examination of the organic phase of the catalyst, the following protocol was employed. After maturation of a system of the type described above under the appropriate atmosphere, the solution was cooled to room temperature, and then sodium carbonate and magnesium sulphate were added to remove any acid and water. The volatiles were then vacuum-transferred to a receiver and examined by GC.

Results

Catalytic activities

A typical catalysis run was carried out with the following standard conditions: reactant concentrations were 0.036 M total ruthenium (from 0.012 mol/liter $Ru_3(CO)_{12}$ initially added), 0.25 M H_2SO_4 and 8 M H_2O in diglyme. The reaction was carried out under a carbon monoxide atmosphere with an initial P_{CO} of 0.9 atm at 100 °C. The reaction vessel had a total volume of *ca.* 100 ml, with the liquid catalysis solution having a volume of 5 ml. This vessel was suspended in a thermostatted oil bath, and the solution stirred vigorously via a small Teflon stirring bar. Solutions of typical runs were bright reddish-orange after initial preparation, reflecting the presence of the $Ru_3(CO)_{12}$ starting material, but after an induction period (*vide infra*) the solution acquired a light yellow colour.

Visual inspection with a strong light showed no cloudiness or turbidity indicative of an inhomogeneous solution, and good stoichiometric agreement of H_2 or CO_2 produced with CO consumed was obtained by GC analysis of the gas phase. First-day turnover frequencies were generally lower than those for a mature catalyst, owing to the induction period; thus turnover frequencies were evaluated for systems which had matured for about 20 h and which had been recharged with fresh CO prior to the reaction period sampled. The reported values are based upon reproducible duplicate runs and represent the average activities of the catalyst solution during the period of maximum performance. The sampling period was chosen to ensure that no more than 15% of the CO present had been consumed. These turnover frequencies (based on the H_2 produced) are assigned an uncertainty of ±15% owing to the uncertainties in the sampling procedures.

An activity profile of a typical run is shown in Fig. 1. Initially, there was very little WGSR activity once the solution was brought to the reaction

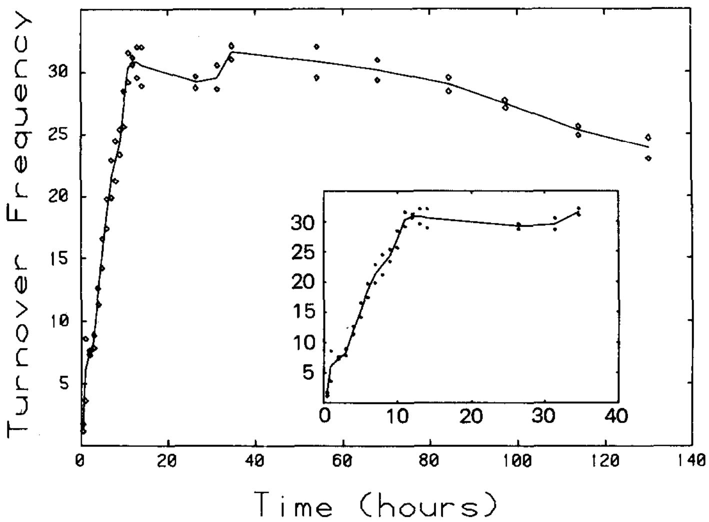


Fig. 1. Plot of turnover frequency (H_2/mol Ru/day) *vs.* time for a typical WGSR run carried out under the following conditions: [Ru] = 0.036 M, P_{CO} = 0.9 atm, T = 100 °C, [H_2SO_4] = 0.25 M, [H_2O] = 8.0 M in diglyme solution.

temperature (100 °C). However, over a period of about 6 - 10 h (the induction period), the activity rose to a level close to the maximum turnover frequency of 30 mol H_2/g-atom Ru/24 h. The catalytic activity remained roughly constant for several days, but then slowly decayed. The lifetime of the catalyst, the system being flushed at least once every 24 h, was 6 - 7 days, after which the initially pale yellow solution had developed a green tinge, and the turnover frequency had dropped substantially. Addition of further amounts of acid or water to these solutions failed to regenerate the catalytic activity. In this context, it is notable that admission of air to hot solutions of an active catalyst caused the irreversible deactivation of the system, suggesting a possible explanation for the slow degradation of the catalyst under normal conditions.

Catalyst solutions prepared from $Ru_3(CO)_{12}$ under the standard conditions but using acidic aqueous 2-ethoxyethanol as the solvent displayed similar characteristics but with reduced catalyst lifetimes. By the time of the third flushing cycle, the solution had become cloudy, its activity had decreased, and copious amounts of red-orange material had sublimed to the cool top of the reaction vessel. This material was shown to be $Ru_3(CO)_{12}$ according to its IR spectrum. DME, THF and methanol all proved to be suitable solvents for the WGSR, showing activities comparable to the diglyme solutions. However, under the standard conditions noted, these solvents also formed much less stable catalyst systems than found with diglyme as the solvent.

Catalyst solutions prepared from $H_4Ru_4(CO)_{12}$ as the initial ruthenium source displayed activities both in diglyme and 2-ethoxyethanol solutions which were virtually identical to those solutions prepared analogously from $Ru_3(CO)_{12}$. For the diglyme solutions, comparable induction periods were noted for both ruthenium clusters, and the mature catalyst solutions were shown to have identical IR spectra. Given that $H_4Ru_4(CO)_{12}$ reacts readily with CO at elevated temperatures to give $Ru_3(CO)_{12}$ [15], the similarity of the two clusters as catalyst precursors is not surprising. However, a somewhat different pattern was seen when the salt $Na_2Ru(CO)_4$ [16] was used as the catalyst precursor. Dissolution of this material in acidic aqueous diglyme under the standard conditions led to an initial burst of H_2 (but not CO_2) formation, due to the reaction of the salt with acid. Furthermore, WGSR activity was noted immediately with no indication of an induction period.

The phosphine-substituted complex $Ru_3(CO)_9(PPh_3)_3$ was also surveyed as a shift reaction catalyst. Heating the initially dark red solution in acidic aqueous diglyme at 100 °C for 18 h afforded a pale yellow solution with a white precipitate and a turnover frequency of 3. During the next 48 h the solution displayed an average turnover frequency of 7, after which the catalytic activity of the solution decayed over a period of 24 h.

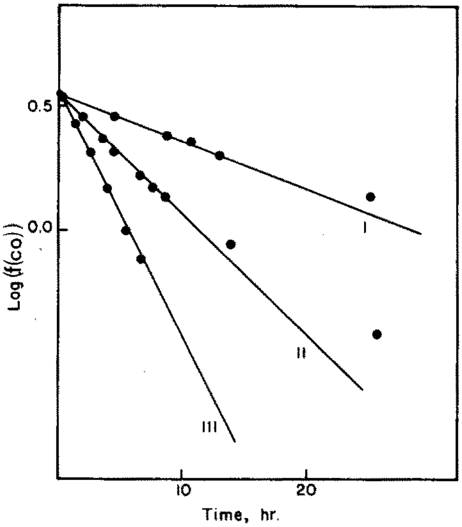
In alkaline solution, it has been shown [8] that catalyst solutions prepared from a mixture of iron and ruthenium carbonyls are significantly more active than catalysts prepared from either iron or ruthenium alone. This synergistic effect has been suggested to be the result of the *in situ* formation of a mixed metal cluster. Accordingly, ruthenium solutions in acid aqueous diglyme were prepared, to which $Fe(CO)_5$ was added such that the ratio of $Fe(CO)_5$:$Ru_3(CO)_{12}$ was either 3:1 or 9:1. The solutions were then conditioned as described above, the turnover frequencies were determined and both found to be, within experimental uncertainties, the same as those expected for the concentration of ruthenium present alone. In independent experiments, both $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were evaluated as WGSR catalysts under the conditions described above, but were found to be inactive. Similarly, $Ir_4(CO)_{12}$, which proved to be a precursor of a WGSR catalyst in alkaline solution [7], is inactive in acid aqueous diglyme solution.

Formate decomposition has been implicated in mechanisms for the WGSR [4]. In order to examine this possible pathway, 1.8 mmol of formic acid was added to an active ruthenium solution at the standard concentrations (P_{CO} = 0.9 atm) in acid aqueous diglyme, and the formation of H_2 and CO_2 monitored by GC analysis. The turnover frequency observed was not significantly different from that of the working catalyst in the absence of formic acid. More significantly, the WGSR stoichiometry continued to be observed, with the CO consumed (836 mmol) equal to the CO_2 produced (829 mmol). Such correspondence implies that this shift reaction catalyst is not significantly active towards formic acid decomposition under these conditions.

The ability of WGSR systems to act as hydrogenation or hydroformylation catalysts has also been documented [3, 17, 18]. Accordingly, the acid-based shift reaction catalyst system was evaluated for such activity [19]. When the CO/CH_4 substrate in a fully matured WGSR system was replaced by an ethylene/CO mixture, neither consumption of ethylene nor production of ethane was observed by GC analysis, and none of the expected products could be detected in the liquid phase. In addition all shift reaction activity had been quenched. Recharging the bulb with the standard CO/CH_4 mixture led to regeneration of the WGSR activity.

Catalyst activities in aqueous diglyme solution as functions of solution parameters

For values of $P_{CO} < 0.9$ atm, the WGSR activity of the ruthenium catalyst was observed to be first order in [CO], as shown by plots of log[CO] *vs.* time (Fig. 2). These were linear over two half-lives, but showed some curvature as the reaction continued. The slopes are dependent upon ruthenium concentration, giving the relative values 1.00, 2.5, and 5.1 for the Ru concentrations 0.018 M, 0.036 M and 0.072 M. These values indicate that the catalysis is first order in ruthenium concentration over this relatively narrow range of conditions. The first-order dependence upon P_{CO}, for values of $P_{CO} < 0.9$ atm, is further demonstrated by Fig. 3, where halving the initial P_{CO} does not affect the slopes of the log[CO] *vs.* time plots,



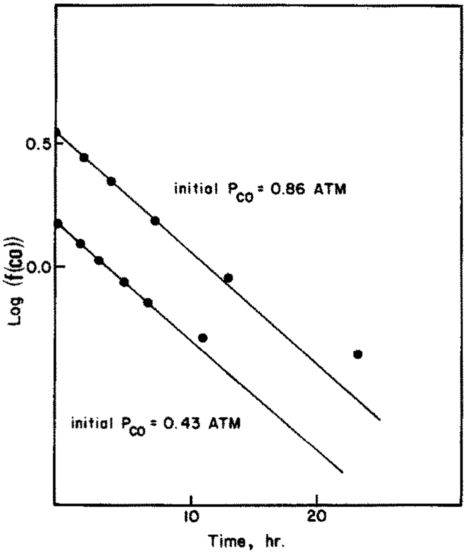


Fig. 2. First-order rate plots for the consumption of CO in a 100 ml batch reactor at 100 °C. Catalyst solutions are 5.0 ml aqueous diglyme with 8.5 M H_2O, 0.5 M H_2SO_4 and the respective ruthenium concentrations, 0.018 M (I), 0.036 M (II), and 0.072 M (III). Initial P_{CO} in each case is 0.9 atm. Slopes of these plots are 1.9×10^{-2} (I), 4.8×10^{-2} (II), and 9.7×10^{-2} (III). f(CO) is a linear function of CO pressure in the reaction vessel dependent on the sampling procedures.

Fig. 3. First-order rate plots for the consumption of CO in a 100 ml batch reactor at 100 °C. Catalyst solutions are 5.0 ml aqueous diglyme with 8.5 M H_2O, 0.5 M H_2SO_4, and [Ru] = 0.036 M. Upper plot is for an initial P_{CO} pressure of 0.86 atm and displays a slope of 4.8×10^{-2} h^{-1}. Lower plot is for an initial CO pressure of 0.43 atm and displays a slope of 4.7×10^{-2} h^{-1}.

although the absolute rate of CO consumption does halve given the same concentration of ruthenium.

The catalyst activities were also relatively insensitive to the H_2SO_4 and H_2O concentrations of the system, when examined by batch reactor techniques for the 'standard' ruthenium concentration (0.036 M) and P_{CO} (0.9 atm). For these conditions, changes in the sulfuric acid and water concentrations over the respective ranges 0.25 - 1.5 M and 4 - 12 M have small effects on the catalysis rates. However, the functionalities were complicated and show concave rate *vs.* concentration curves, with maximum rates found at 4 M H_2O and 0.5 M H_2SO_4. (Notably, flow reactor studies in progress show greater sensitivities to these reaction parameters when significantly different $[Ru]_{total}$ and P_{CO} values were employed [20].)

Titration of mature active solutions showed no net consumption of acid. However, the activity of the system was found to be sensitive to the nature of the acid used, with sulfuric acid giving the highest activity among those studied. The use of other acids under otherwise standard conditions resulted in activities roughly an order of magnitude lower. The approximate turnover frequencies were oxalic acid (3), H_3PO_4 (2), CF_3CO_2H (2), fumaric acid (2), succinic acid (1), acetic acid (1), and malonic acid (1). The stronger acids appear to give greater activities, and there is no special advantage apparent for acids with a chelating conjugate base. The activities noted for fumaric and maleic acids were for CO_2 production, given that H_2 formation was much smaller, suggesting some reduction of the double bond in the acid. However this question was not pursued further.

The activity of the catalyst system under the standard concentrations was found to be temperature-sensitive. A linear Arrhenius plot of the slopes of log[CO] plots *vs.* time over the temperature range 90 - 140 °C gave an apparent activation energy of 14 kcal/mol. A similar activation energy was measured by flow reactor techniques under otherwise similar conditions [20].

As previously noted, the activity of the shift reaction catalyst increases linearly with increasing P_{CO} at values of $P_{CO} < 0.9$ atm; however, at higher P_{CO} values the activity levels off and then decreases, as shown in Table 1. Such behaviour is observed not only for runs initiated at high P_{CO}, but is also seen for working systems which are perturbed by changing P_{CO}. For example, when the pressure of CO in a catalytic solution which had been matured for 24 h was increased from 0.9 atm to 2.7 atm, (at 100 °C) the colour of the solution changed from pale yellow to dark orange over a period of 1.5 h, and the system was found to have a residual turnover frequency of 4 mol H_2/mol Ru/day, compared to a previous value of 30 mol H_2/mol Ru/day. Upon cooling the solution to room temperature, $Ru_3(CO)_{12}$ was rapidly deposited (identified by IR), and could be recovered by filtration in amounts exceeding 80% of the amount initially added to the system. A ^1H NMR spectrum showed no evidence for the formation of formic acid in the supernatant of catalytic solutions deactivated by running at high pressures of CO.

TABLE 1

Variation of catalytic activity with P_{CO}[a]

P_{CO} (atm)	Turnover frequency[b]
0.3	7.0
0.6	17.0
0.9	30.0
3.2	4.2
6.6	1.1

[a] Standard conditions are [Ru] = 0.036 M, 8 M H_2O, 0.25 M H_2SO_4 in diglyme at 100 °C.
[b] Turnover frequency is defined as mol H_2 produced/mol ruthenium/day.

Solutions that had been deactivated by running at high P_{CO} showed reversible behaviour. When the pressure in such systems was reduced to 0.9 atm (at 100 °C), the activity of the system returned to its previous value, although an induction period of several hours was observed. This cycle could be repeated over the life of the catalyst.

As noted above, the WGSR catalysis activity of newly-prepared solutions displays an induction period of 6 - 10 h under the standard conditions. During this period, the initially orange solution becomes pale yellow, and the activity of the solution increases steadily until full acitivity is reached. When $Ru_3(CO)_{12}$ was heated in acid aqueous diglyme to 100 °C under a blanket of either H_2 or N_2 (0.9 atm) for 18 h and then the gas-phase component replaced by the CO/CH_4 mixture, no induction period for catalytic activity is seen and the solution reaches full activity in less than 1 h.

Attempts to precipitate characterizable ruthenium species from acidic aqueous diglyme solutions by addition of various cations or anions and/or the additon of water were fruitless, as were attempts to isolate definable species by removal of the solvent *in vacuo*. However, it is noteworthy that if an active solution were set aside for a period of 4 - 7 days at room temperature under a CO atmosphere, $Ru_3(CO)_{12}$ slowly precipitated from the solution. Generally about 95% of the initially-added ruthenium could be recovered.

Spectroscopic observation of active solutions

The goal of these studies was to discern the spectral characteristics of the catalysis solutions under working conditions. To this end, *in situ* spectral investigations were carried out using UV–vis and IR spectrophotometry as well as ^1H and ^{13}C NMR spectroscopy at temperatures and P_{CO} values where WGSR activity is evident.

Electronic spectra

The orange-to-yellow colour change which occurs during the induction period was examined more closely by UV–vis spectrophotometry. The initial orange solution of $Ru_3(CO)_{12}$ displays a band with a λ_{max} at 392 nm. After the induction period, the solution is yellow and shows no such bands in the visible region; these spectral changes are shown in Figure 4. The foregoing observations were made with a ruthenium concentration of 0.0036 M in 1 mm-pathlength quartz cells.

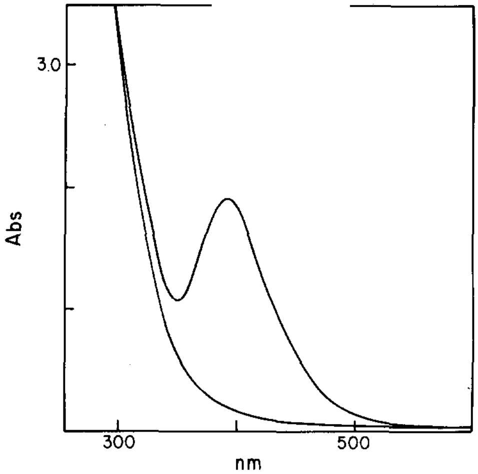


Fig. 4. Electronic spectra (0.10 cm cell) of a catalyst solution prepared from $Ru_3(CO)_{12}$ ([Ru] = 3.6×10^{-3} M), 0.5 M H_2SO_4, 8.0 M H_2O and P_{CO} = 0.9 atm in diglyme at 100 °C. The upper curve represents the spectrum 5 min after the solution was prepared at this temperature; the lower curve is the spectrum after 6 h.

IR spectra

The IR spectra were recorded in the high-temperature cell described in the Experimental section. A 100 °C solution of $Ru_3(CO)_{12}$ in diglyme displayed a spectrum consisting of three bands; 2060 , 2036, and 2010 cm^{-1}, similar to the room temperature spectrum of $Ru_3(CO)_{12}$ in THF. The same IR bands were noted in acid aqueous diglyme when a solution of $Ru_3(CO)_{12}$ was heated at 100° under CO (0.9 atm) for only 15 min. However, the resulting IR spectrum displayed an additional band at 2086 cm^{-1} which may be attributed to decomposition reactions (*vide infra*).

In order to investigate the IR spectrum of a working catalyst, a standard reaction mixture which had been matured overnight in a 100 ml reaction vessel (P_{CO} = 0.9 atm, T = 100 °C), and shown to be active for the WGSR, was transferred via cannula to the high-temperature cell, and the spectrum recorded at 100 °C under 0.9 atm CO. Initially the spectrum showed two strong bands at 2050 and 1961 cm^{-1}, although over a period of 2 - 3 h bands at 2086 and 2014 cm^{-1} appeared at the expense of the former bands. Since the initial bands at 2050 and 1961 cm^{-1} have been reproducibly observed with the same proportional intensities in various spectra, it appears that these are closely coupled and represent key spectral features of a single species denoted as I. Similarly the bands at 2086 and 2014 cm^{-1} appear to derive from a distinct species denoted as II.

The high-temperature cell was also used to recorded the IR spectrum of a WGSR solution which had been partially deactivated by high partial pressures of CO. In this respect the high-temperature cell played a key role, as all other attempts to obtain such a spectrum had been frustrated by the rapid precipitation of $Ru_3(CO)_{12}$ from such solutions when cooled to ambient temperatures. A key question is whether the $Ru_3(CO)_{12}$ is formed from another species upon cooling or is present in the catalyst solution. The IR spectrum of a working catalyst which had undergone high pressure (P_{CO} = 2.74 atm) deactivation for 2 h exhibited bands arising from $Ru_3(CO)_{12}$ (bands at 2060, 2035 and 2010sh cm^{-1}) together with bands from I and II. Solutions which had undergone a longer deactivation period showed bands arising predominately from $Ru_3(CO)_{12}$, with I and II as minor components.

In experiments to ascertain the necessary components for the formation of the active catalyst system, a WGSR mixture was prepared without the addition of H_2SO_4. After heating for 18 h the solution was dark orange and its IR spectrum displayed only bands arising from $Ru_3(CO)_{12}$. In contrast, the IR spectrum of an acid aqueous diglyme WGSR mixture matured under either H_2 or N_2 initially showed bands consistent with the presence of I and relatively small amounts of II. However, prolonged heating in the high-temperature IR cell (2 - 3 h) caused the bands arising from II to predominate.

In subsequent experiments to delineate the origin of the species II, an active WGSR solution was degassed by two freeze–pump–thaw cycles and air admitted to the evacuated bulb, which was then heated for 4 h at 100 °C, during which time the yellow colour became considerably less intense. The IR spectrum of this solution showed only the bands at 2086 and 2014 cm^{-1}, implying that complex II is the predominant metal carbonyl of significant concentration present.

The *in situ* IR experiments may be summarized as follows. Under WGSR catalysis conditions ([Ru] = 0.036 M, P_{CO} = 0.9 atm, and T = 100 °C in acid aqueous diglyme), a mature active solution displays bands attributable to a single metal carbonyl species I. The same species is generated in solutions matured for 18 h under either H_2 or N_2, but is not generated in the absence of water. Simple dissolution of $Ru_3(CO)_{12}$ in the hot acidic aqueous diglyme mixture under CO does not lead to major changes in the spectrum, indicating that the induction period noted above involves slow transformation of the inactive triruthenium cluster to other species. Under high CO pressures, $Ru_3(CO)_{12}$ is distinctly present in matured catalyst solutions, consistent with the lowered activities under such conditions. Lastly, the second species II noted in various spectra appears to be a 'decomposition' product, probably resulting from reaction with O_2, given that only II is found in solutions deliberately exposed to air at elevated temperatures and that attempts to regenerate the activities of these solutions by reheating under CO proved unsuccessful.

^{1}H *NMR spectra*

The proton NMR spectrum of an active WGSR solution recorded at 100 °C under 0.9 atm of CO exhibited two peaks at δ −14.05 and −19.07 in the ratio 2.5:1. When cooled to 25 °C, this solution showed bands at δ −13.60, −13.90, and −19.07, the integrated intensity of the former two peaks to the latter being 2.3:1. When reheated to 100 °C, the original spectrum was regenerated. Air was then admitted to the solution, and the spectrum recorded after 1 h at 100 °C showed these two peaks in the ratio 1.15:1. After cooling the solution to 25 °C the spectrum showed peaks at δ −13.06, −13.90, and −19.07, with the intensity of the two low-field peaks to the high-field one being 1.5:1. Solutions of $Ru_3(CO)_{12}$ matured in acid aqueous diglyme under either H_2 or N_2 exhibit essentially the same high-temperature spectrum as noted above, but only a single lower-field peak (δ −13.90) was observed upon cooling to 25 °C, a result which suggests that the resonance at δ −13.60 represents a separate species requiring the presence of CO. The above results imply that the δ −19.07 resonance arises from a decomposition product, and that the δ −14.05 peak derives from the catalytically active species.

^{13}C *NMR spectra*

The natural-abundance ^{13}C NMR spectra were recorded using the same conditions described for the ^{1}H NMR spectra. At 100 °C an active WGSR solution displays a single peak in the ^{13}C spectrum at 198.3 ppm, while in the ^{1}H-coupled spectrum this peak is split into a doublet (J ^{1}H–^{13}C = 10 Hz). When cooled to 25 °C, other resonances at 202.8 and 197.8 ppm were noted, but the original peak at 198.3 ppm predominates. Finally the solution was cooled to −55 °C, where the signal became broader but no further multiplicity was observed, implying that the complex under observation is fluxional at that temperature, since it appears unlikely that all COs of the proposed species are structurally equivalent (*vide infra*).

Discussion

The foregoing results demonstrate that solutions prepared from $Ru_3(CO)_{12}$ in acidic aqueous diglyme (or other ethereal/alcoholic solvents) form a homogeneous catalyst for the water–gas shift reaction under relatively mild conditions. Shift reaction catalysis in basic solutions appears to be a general reactivity property of metal carbonyls; however, the present system represents one of the few examples of such catalysis in acidic media. Notably, neither iron nor iridium carbonyls form active solutions under similar acidic conditions (see Results).

It is clear from the nature of individual catalysis runs that $Ru_3(CO)_{12}$ itself is not the species directly responsible for the activation of CO in the WGSR cycle. No $Ru_3(CO)_{12}$ is observable by IR, ^{13}C NMR, or UV–vis spectral studies of operating catalysts in acidic aqueous diglyme under the standard conditions ($P_{CO} < 1$ atm). This observation alone would not discount the possible role of $Ru_3(CO)_{12}$ in a WGSR cycle; however, the added observation that the increase in the solution's activity during the induction period parallels the disappearance of $Ru_3(CO)_{12}$ indicates that the trinuclear cluster is merely a precursor of the active species. Furthermore, the decreased WGSR activity at high P_{CO} occurs with the corresponding appearance of $Ru_3(CO)_{12}$ under these conditions. Therefore the induction period represents the relatively slow formation of the active ruthenium species from $Ru_3(CO)_{12}$.

The presence of CO is not a prerequisite for forming the active species, given that solutions matured overnight under either an H_2 or N_2 atmosphere displayed no appreciable induction period for WGSR activity upon charging the reaction vessel with CO (0.9 atm). Both IR and NMR spectra of these H_2- or N_2-matured solutions show the major ruthenium carbonyl species present to the identical or very closely related to those present in the working catalyst.

The UV–visible spectral properties of the working catalyst strongly indicate that the induction period involves the conversion of the initial ruthenium cluster to species of lesser nuclearity. Solutions prepared from $Ru_3(CO)_{12}$ are initially a deep reddish-orange, but fade to pale yellow over the induction period. The spectrum of the active catalyst shows no evidence of the 392 nm band characteristic of $Ru_3(CO)_{12}$, nor any other absorption band in the near UV or visible regions. Given that such bands are characteristic of ruthenium clusters and have been assigned at σ–σ^* transitions of cluster metal–metal bond frameworks [21], the absence of such absorption indicates that the ruthenium carbonyl species present in working catalyst solutions are either mononuclear or dinuclear complexes.

The ^1H NMR spectra of working catalyst solutions recorded under CO in acidic aqueous diglyme at 100 °C indicate the presence of two hydride-containing species: the major component I′ displays a hydrogen resonance at δ −14.05 but another species, II′, with a hydrogen resonance at δ −19.07 is present. Since the latter signal increases significantly when air is deliberately introduced into the solution, we may conclude that II′ is an oxidation product of I′. Similarly, the *in situ* IR spectra indicate the presence of one major carbonyl species, I, with strong ν_{CO} bands at 2050 and 1961 cm^{-1} in the working catalyst. Exposure to air leads to the formation of a second species, II, with strong ν_{CO} bands at 2086 and 2014 cm^{-1} at the expense of I. Circumstantial evidence thus suggests that I and I′ are the same species as are II and II′, and that II is a product of the air oxidation of I*. (In further support of this conclusion is the observation that ν_{CO} bands of II appear at higher frequency than those of species I.) Comparison of the ^1H NMR resonance at δ −14.05 to those in Table 2 for various ruthenium carbonyl

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*An alternative is the suggestion made by a referee that the oxidation product may be the result of reaction with acid, *e.g.*, $RuH^+ + H^+ \rightarrow Ru^{2+} + H_2$. While this might explain long-term deactivation processes, it is clear that exposure to oxygen does lead to the rapid, irreversible deactivation of hot catalyst solutions.

TABLE 2

^1H and ^{13}C NMR data for ruthenium carbonyl complexes

Complex	^{13}CO (ppm)	^1H (δ)	$J\ ^1H-^{13}C$ (Hz)	Reference
$[Ru_4(CO)_{13}]^{2-}$	223.7[a]	—	—	26
$[H_2Ru_4(CO)_{12}]^{2-}$	220.0[b]	−19.3	10.3 (*trans*) 5.9 (*cis*)	27
$[HRu_4(CO)_{13}]^-$	203.7[a]	−15.8	—	26
$[HRu_3(CO)_{11}]^-$	204.8[c]	−12.6	6 (average)	1
$[H_3Ru_4(CO)_{12}]^-$	198.2[b]	−17.0	7.3	26
$[HRu(CO)_4]^-$	—	−7.0[d]	—	28
$HRu_3(CO)_{10}NO$	202.9, 195.5[a] 194.5, 185.8	−11.9		29
$Ru_3(CO)_{12}$	198.0[e]	—	—	22
$H_2Ru(CO)_4$	192.5[f] 190.1	−7.6	7 (*cis*)	30
$[HRu(CO)_5]^+$	180.4[g] 178.4	−7.2	4 (*cis*) 24 (*trans*)	31
$[HRu(CO)_4P(C_6H_5)_3]^+$	185.6[g] 183.3 182.9	−6.53	4 (*cis*) 24 (*trans*) < 2 (*cis*)	31
$[HRu_3(CO)_{12}]^+$	191.0, 188.0[g] 184.5, 178.9	−19.8	—	32

[a] Solvent $CD_2Cl_2/CHClF_2$.
[b] Solvent THF-d_8.
[c] Solvent CD_3OD.
[d] Solvent $(CD_3)_2CO$.
[e] Solvent $CDCl_3$.
[f] Solvent $C_6D_5CD_3$.
[g] Solvent conc. H_2SO_4.

hydrides shows that this value falls within the range (δ −11.9 - −19.8) noted for bridging hydrides, and is considerably higher-field than found for the three mononuclear ruthenium carbonyl hydrides ($\delta \sim -7$). The fact that the 198.3 ppm resonance seen in the ^{13}C NMR spectrum is split into a doublet when the spectrum is recorded in the ^1H-coupled mode indicates the presence of but a single hydride coupled equally to all the carbonyl ligands. (The apparent equivalence of the carbonyls in this spectrum is not unexpected given the fluxional nature of ruthenium carbonyl clusters at elevated temperatures [22].)

Although the measurements described above were plagued on occasion by the presence of the redox product II, we conclude from these studies that the spectral observations under the standard conditions (0.036 M total Ru, 0.25 M H_2SO_4, 8 M H_2O and P_{CO} = 0.9 atm) are consistent with the large majority of the ruthenium of the active catalyst solution being present as a single species I. Furthermore, we conclude that this species has a nuclearity less than three, has one bridging hydride and is fluxional over the temperature range −55 - +100 °C. The presence of a bridging hydride narrows the range of possibilities to dinuclear complexes. In a preliminary report [23] we further argued that the ^{13}C NMR resonance suggests that I may be the unknown species $[HRu_2(CO)_8]^-$. However, based on a key comparison to the acid/base properties of the $[HOs_2(CO)_8]^-$ anion, we now conclude that the latter speculation was very likely in error. Jordan and Norton [24] have recently established that in acetonitrile $[HOs_2(CO)_8]^-$ is two orders of magnitude more basic than Et_3N. Since the acid/base properties of analogous ruthenium and osmium carbonyl complexes are generally similar [25], the $[HRu_2(CO)_8]^-$ anion would be too basic to be the predominant ruthenium species in solution. Given that a substituted derivative, *e.g.* $[HRu_2(CO)_{8-y}(OR_2)_y]^-$ (where OR_2 = water, diglyme or bisulphite), would be expected to be even more basic [25], we must conclude that a *reduced* ruthenium hydride species cannot be the dominant species present.

The alternative dinuclear monohydride would be a derivative of the cation $[HRu_2(CO)_9]^+$, *e.g.* $[HRu_2(CO)_{9-x}(OR_2)_x]^+$ (OR_2 = diglyme or water). The chief argument against such a species would be that the ^{13}C chemical shift observed for I was significantly downfield of those seen for the hydrides $[HRu_3(CO)_{12}]^+$, $[HRu(CO)_5]^+$ and $[HRu(CO)_4(PPh_3)]^+$ in sulphuric acid solvent (Table 2) [26 - 32] and falls in the range observed for neutral and monoanionic carbonyls. However, it should be noted that substitution of a carbonyl by a ligand which is a poorer π-acid leads to a downfield shift in the ^{13}C resonance (see Table 2 for a comparison of the $[HRu(CO)_5]^+$ and $[HRu(CO)_4(PPh_3)]^+$ spectra). Therefore $[HRu_2(CO)_{9-x}(OR_2)_x]^+$ would be expected to display ^{13}C resonances considerably downfield from the parent cation.

Several key observations regarding the transformation of $Ru_3(CO)_{12}$ to the species I must be considered in evaluating the nature of the latter. First, heating $Ru_3(CO)_{12}$ under CO (0.9 atm) for 18 h at 100 °C in aqueous diglyme (8.0 M H_2O) but without the addition of acid leads to no color change, and the IR spectrum at 100 °C shows the only species in solution to be $Ru_3(CO)_{12}$. Additionally, when allowed to cool to room temperature, such solutions rapidly precipitate $Ru_3(CO)_{12}$ quantitatively. On the other hand, heating an anhydrous acidic diglyme solution (0.25 M H_2SO_4) solution under CO (0.9 atm) leads to the transformation of the starting material into a new species with an IR spectrum markedly different from that of I. Second, heating $Ru_3(CO)_{12}$ in the standard aqueous acidic diglyme solvent but under a high pressure of CO (P_{CO} = 2.74 atm) prevents the transformation of $Ru_3(CO)_{12}$ into I. Lastly, when a mature working catalyst (predominantly I under the standard conditions) is then operated at increased CO pressure (2.74 atm), the system undergoes a color change from yellow to orange-red, paralleled by the appearence of the IR bands characteristic of Ru_3-

$(CO)_{12}$. Cooling of these solutions leads to the rapid precipitation of $Ru_3(CO)_{12}$.

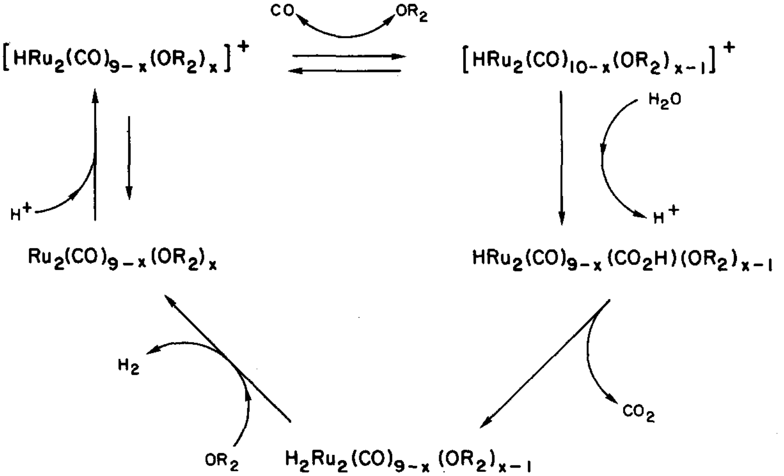
The effect of P_{CO} on the equilibrium between I and $Ru_3(CO)_{12}$ indicates that the CO/Ru ratio in I is less than that of $Ru_3(CO)_{12}$, *i.e.*, <4. Thus if $[HRu_2(CO)_{9-x}(OR_2)_x]^+$ is the correct formulation, then the relevant equilibrium would be eqn. 4, where x must be two or greater:

$$[HRu_2(CO)_{9-x}(OR_2)_x]^+ + (x-1)CO \rightleftharpoons (2/3)Ru_3(CO)_{12} + H^+ + xOR_2 \quad (4)$$

If one considers the manner by which the catalyst activity is decreased by high P_{CO} (see Results and below), one must further conclude that x must indeed be three or greater.

In Scheme 1 a catalytic cycle is proposed based upon the conclusion that the predominant ruthenium species under the optimum conditions for catalysis is $[HRu_2(CO)_{9-x}(OR_2)_x]^+$ ($x \geqslant 3$). The first-order dependence on P_{CO} at pressures less than 1 atm is suggested to be the result of the substitution of CO for OR_2 on I prior to H_2O addition to a carbonyl of the resulting species. The inhibition of the catalysis by high pressures of CO is attributed to the shift in the equilibrium denoted in eqn. 4 toward $Ru_3(CO)_{12}$, removing ruthenium from the reservoir of active species. Given that the decrease in activity at $P_{CO} > 0.9$ atm is roughly inverse second order in P_{CO}, these observations suggest that $x = 3$, although given the complex equilibria undoubtedly present in this system, a value larger than 3 might also be reasonable.

The relative insensitivity of the reaction to the acid and water concentrations is somewhat puzzling; however, it should be noted that extensive kinetic studies of this system using flow reactor techniques confirm the relative insensitivity of the system to these parameters under the conditions employed here for batch reactor studies. The preliminary data from the flow reactor studies also indicate that, at P_{CO} much greater than 1 atm, increasing



Scheme 1.

$[H_2SO_4]$ increases the measured activity. As a consequence, the P_{CO} at which maximum activity is observed shifts somewhat to higher values with increasing $[H_2SO_4]$. An explanation for this phenomenon can be found in the origin of the high-pressure CO inhibition of the WGSR activity, namely eqn. 4. Under a P_{CO} where $Ru_3(CO)_{12}$ is present at significant concentrations in equilibrium with the active species, this equilibrium would be markedly affected by the acid, with increased $[H^+]$ favouring the formation of cationic species such as $[HRu_2(CO)_{9-x}(OR_2)_x]^+$.

The flow reactor studies [20] also give some indication of the role of mononuclear complexes in the reaction medium. Although catalysis runs at ruthenium concentrations comparable to the batch reactor conditions were (within experimental uncertainty) first-order in [Ru], runs carried out at ruthenium concentrations an order of magnitude lower displayed higher order kinetics approaching second order. Furthermore, a serious complication of such kinetics studies was the loss of ruthenium swept from the catalysis solutions by the flowing substrate gas. Analysis of the material captured in a low-temperature downstream trap indicates the ruthenium to be present as the mononuclear species $Ru(CO)_5$. Thus these preliminary flow reactor data are consistent with a dinuclear species (*e.g.* I) as the active catalyst and the competing equilibria leading to less active mononuclear and trinuclear complexes.

Our continuing studies of this system include a detailed kinetic study of the WGSR by flow reactor techniques. In addition, we are examining the reactions and properties of various ruthenium carbonyl complexes in acidic media, with the goal of modelling individual steps in the proposed WGSR mechanisms as well as other processes concerned with CO activation under such conditions.

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