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Homogeneous Catalysis of the Water Gas Shift Reaction by Ruthenium and Other Metal Carbonyls. Studies in Alkaline Solutions

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Abstract: Homogeneous catalysis of the water gas shift reaction ($H_2O + CO \rightleftharpoons H_2 + CO_2$) has been demonstrated for a number of metal carbonyl complexes under alkaline conditions. Characterization of the catalysts based on ruthenium carbonyl in alkaline, aqueous ethoxyethanol solution demonstrates that the principal species present under the reaction conditions are the carbonyl hydride anions $H_3Ru_4(CO)_{12}^-$ and $HRu_3(CO)_{11}^-$. (The room temperature synthesis of the latter ion by the reaction of $Ru_3(CO)_{12}$ in alcoholic KOH is described.) The catalysis rate shows a first-order dependence on both the CO partial pressure and the total ruthenium concentration. Cyclic mechanisms proposed to explain these observations involve nucleophilic attack of water or of hydroxide on coordinated CO followed by decarboxylation to give hydridic species from which H_2 is eliminated in a CO-assisted, rate-limiting step. It is noted that catalysts prepared by adding both iron and ruthenium carbonyls to the same solution are more active than either the ruthenium-based or the iron-based catalysts alone. These mixed metal catalyst solutions are shown to contain mixed metal clusters, and it is proposed that the synergetic effect on catalytic activity may result from greater reactivity of the mixed metal clusters toward elimination of dihydrogen.

Introduction

The reaction of carbonaceous materials with water at high temperatures (normally achieved by partial oxidation) produces a mixture of water, carbon monoxide, carbon dioxide, and dihydrogen, i.e., water gas. The key components are CO and H_2, and methods of activating the reactions of each of these individually as well as in a concerted fashion to produce methane, methanol, Fischer-Tropsch products, etc., have long been major goals of catalysis research. Notably, such processes are essential to the production of gaseous and liquid fuels from coal. A key reaction in such schemes is the water-gas shift reaction (WGSR):

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

since this reaction finds applications for the production of dihydrogen and for the adjustment of H_2/CO ratios in feed mixtures for some of the reactions noted above. Commercial methods for carrying out the shift reaction involve heterogeneous metal oxide catalysts at elevated temperatures.[1] Based upon the thermodynamics of the WGSR,[2] catalysts active at low temperatures would lead to greater reaction efficiency and smaller thermal inputs. In this context, homogeneous catalysts, particularly those which can be immobilized such as in a supported liquid-phase reactor,[3] may find practical applications.

Interest in the possible homogeneous catalysis of the shift reaction has surfaced intermittently over the past 4-5 decades,[4] and the observation of H_2 and/or CO_2 as minor side products in the homogeneously catalyzed carbonylations of several organic substrates had been inferred to result from catalyses of the WGSR.[4c] However, the first clear-cut demonstration of catalysis specific for the WGSR and based upon definable metal complexes was reported only recently. In 1977, three such reports were made. From these laboratories we reported[5] that ruthenium carbonyl in alkaline aqueous ethoxyethanol is a catalyst for the WGSR under relatively mild conditions (100 °C, <1 atm CO). The other reports were by Eisenberg and co-workers,[6] who described a homogeneous catalyst based upon the rhodium(I) complex $[Rh(CO)_2Cl]_2$ in acetic acid/HCl/NaI medium, and by Pettit and co-workers,[7] who described catalysis by several metal carbonyls plus trimethylamine. Additional WGSR catalysts based on metal carbonyl complexes in alkaline solution,[8-10] in amine solutions,[8] and in acidic solutions[8] have now been described as well as two catalysts based on mixed metal complexes[8,11] and a platinum phosphine catalyst.[12] Thus it appears that catalysis of eq 1 can be effected by a surprisingly wide range of metal complexes and under markedly different medium conditions.[8a]

Described here are the details of further investigations of the catalysis by ruthenium carbonyl and by other metal carbonyls in alkaline solutions. These studies of possible WGSR catalysts drew inspiration from much earlier work where the reactions of metal carbonyls with hydroxide and weaker bases such as amines and water were shown to give metal carbonyl anions and metal carbonyl hydrides,[13] e.g.[14]

$$Fe(CO)_5 + Ba(OH)_2 \rightarrow Fe(CO)_4H_2 + BaCO_3 \qquad (2)$$

Since hydrides can be induced to (reductively) eliminate dihydrogen, such carbonyl activation by nucleophiles forms a key step in a hypothetical catalytic cycle (Scheme I) which served as a working proposal for our initial studies in alkaline solution. Notably, ample precedent[15-20] exists for the key steps

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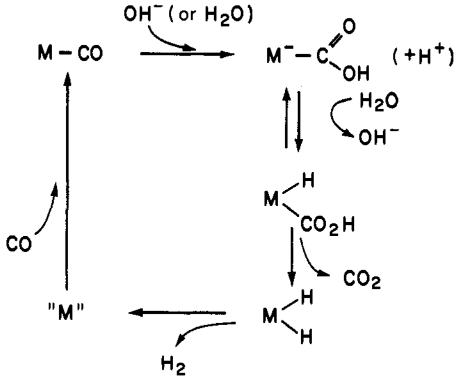
Scheme I



of this hypothetical scheme, where M is a mononuclear or polynuclear metal complex.

Experimental Section

Reagents. Prior to use, 2-ethoxyethanol (obtained from Aldrich and Mallinckrodt) was distilled from anhydrous stannous chloride followed by distillation from magnesium turnings. Dilut-It analytical concentrate, titrated prior to use, served as the source of carbonate-free potassium hydroxide and was stored in a standard carbon dioxide free storage vessel. The 94/6 carbon monoxide/methane mixture, prepurified grade, was obtained from Linde. The metal carbonyls $Ru_3(CO)_{12}$ and $Re_2(CO)_{10}$ were obtained from Strem Chemicals, $Ir_4(CO)_{12}$ was from Pressure Chemical, and $Fe(CO)_5$ was from Alfa Inorganics. The following metal carbonyls were synthesized by previously reported methods: $Ru_3(CO)_{12}$,[21] $Ru_6C(CO)_{17}$,[22] $H_4Ru_4(CO)_{12}$,[23] $H_2Ru_4(CO)_{13}$,[24] $H_2FeRu_3(CO)_{13}$,[24] $Rh_6(CO)_{16}$,[25] and $H_3Re_3(CO)_{12}$.[26]

The salt $(Et_4N)[HRu_3(CO)_{11}]$ was prepared as follows. To solid $Ru_3(CO)_{12}$ (0.27 g) under a CO atmosphere were added 2-ethoxyethanol (13 mL), water (1.8 mL), and 6.6 M aqueous KOH (0.3 mL). The mixture was stirred at ambient temperature for 3 h, during which time the $Ru_3(CO)_{12}$ dissolved completely to give a deep red solution. To this was added a twofold excess of solid $[Et_4N]Cl{\cdot}H_2O$ plus water to effect precipitation of a dark red solid. This solid was collected by filtration, then washed with water followed by cyclohexane until the filtrate was colorless. Recrystallization from dichloromethane/petroleum ether (35-60 °C) gave dark purplish red crystals (0.22 g, 70% yield overall). Anal. Calcd for $[Et_4N][HRu_3(CO)_{11}]$, $C_{19}H_{21}O_{11}NRu_3$: C, 30.72; H, 2.83; N, 1.88. Found: C, 30.84; H, 2.88; N, 1.91.

Apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Proton and carbon-13 nuclear magnetic resonance spectra were recorded on Varian XL-100 and Bruker HFX-10 spectrometers, respectively, operating in the pulsed mode. UV-visible spectra were recorded on a Cary 118C recording spectrometer. Gas sample analyses were performed on a Hewlett-Packard 5830A programmable gas chromatograph, calibrated for the appropriate substrates. The columns used were Poropak Q (mesh 80-100) columns obtained from Hewlett-Packard and the carrier gas used was a Linde prepared 8.5% H_2/91.5% He mixture. Gas samples were taken with Analytical Pressure Lok gas syringes obtained from Precision Sampling Corp. Calibration curves for the chromatographs and sampling procedures were prepared periodically for CO, CO_2, and H_2 for gas sample sizes ranging from 0.05 to 1.5 mL STP of the gas. These calibration curves were linear for CO and CO_2 but not for H_2. The validities of the calibrations were checked by analyzing known gas mixtures prepared in glass bulbs on a vacuum system, and analyses were found accurate and reproducible to within ±5% of the analyzed value within the typical range of gas compositions studied in catalysis runs.

Methods for the Preparation of Catalytic Runs and Analysis of Gas Samples. The all-glass reactor vessel (100 mL) consisted of a round-bottom flask with two stopcock side arms, angled slightly away from one another. One side arm served for attachment to the vacuum line and the other, capped with a serum cap, allowed for periodic gas-phase sampling. Typically, to the metal carbonyl in the vessel, 2-ethoxyethanol and water were added in succession. The reactor vessel was then attached to the vacuum line possessing an attached manometer and carbon monoxide and hydrogen inlets. The solution was degassed by subjection to two freeze-pump-thaw cycles using an acetone/dry ice slush bath as coolant, after which time the system was charged with CO (~1 atm). The aqueous KOH solution was then added to the solution by syringe through the serum cap and the solution was stirred for several minutes. After an additional freeze-pump-thaw cycle, the system was charged with CO at the desired pressure. The vessels were suspended in thermostated oil baths and the solutions stirred magnetically. The systems were periodically flushed and recharged with CO in a manner similar to that previously described for the initiation of a run. Gas samples were periodically removed at bath temperature by gas syringe through the serum capped stopcock side arm. The reaction stoichiometries were analyzed with methane (6.00 mol % of the CO/CH_4 mixture) serving as an internal calibrant. The CO/CH_4 area ratio for the unreacted mixture, coupled with the known quantity of the initial amount of moles of CO and the gas-phase component percentages, allows for the calculation of the absolute quantities of H_2 and CO_2 produced, along with the amount of CO consumed. Quantities of CO found by comparison to the CH_4 internal calibrant compared favorably with those found by direct comparison to calibration curves. The amounts of H_2 and CO_2 produced were corrected for very small background signals noted when gas samples from control reactions in the absence of added catalyst were analyzed.

Table I. WGSR Activities of Various Metal Carbonyl Catalysts in Alkaline Aqueous Ethoxyethanol Solution[a]

initial complex[b]	H_2 activity[c]	CO_2 activity[c]	A_{H_2}
$H_2FeRu_3(CO)_{13}$	10.3	10.9	2.6
$Ir_4(CO)_{12}$	5.6	6.6	1.4
$H_2Ru_4(CO)_{13}$	4.4	4.0	1.1
$H_4Ru_4(CO)_{12}$	3.7	3.3	0.9
$Ru_3(CO)_{12}$	2.8	2.7	0.9
$Ru_6C(CO)_{17}$	1.5	1.9	0.25
$Fe(CO)_5$	1.0	1.1	1.0
$Rh_6(CO)_{16}$	0.8	1.3	0.13
$H_3Re_3(CO)_{12}$	0.12	0.06	0.04
$Re_2(CO)_{10}$	0.06	0.10	0.03

[a] T = 100 °C, P_{CO} = 0.9 atm; reaction carried out in all-glass vessels, stirred magnetically. [b] Solutions prepared from 0.04 mmol of complex (0.012 M), 2 mmol of KOH (0.6 M), 0.02 mol of H_2O (6 M), and 3 mL of 2-ethoxyethanol. [c] Represents average for a number of daily runs; uncertainty ±15%. Activity is mol gas (mol complex)$^{-1}$ (day)$^{-1}$. [d] Normalized activity in mol H_2 (g atomic wt metal)$^{-1}$ (day)$^{-1}$.

Results

Activities in KOH Solutions. Table I lists turnover numbers (based on H_2 production) for the catalysis of the shift reaction by several metal carbonyl complexes in alkaline aqueous ethoxyethanol. The solution conditions include an initial 0.6 M concentration of KOH (see below), P_{CO} = 0.9 atm, and T = 100 °C. The homogeneity of the systems is suggested by a number of points. In all cases the solutions appear clear (no turbidity) when examined visually with a strong light. Furthermore, subjection of several systems including $H_2FeRu_3(CO)_{13}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$, $Ru_6C(CO)_{17}$, and $Fe(CO)_5/Ru_3(CO)_{12}$ to filtration of the catalyst solution through a Millipore filter (FH; 0.5 μm pore size) under a nitrogen atmosphere resulted in no loss in the H_2 production rate within experimental uncertainty. Also, reaction rates were reproducible among different batches of catalyst. Analysis of the GC data, with methane serving as an internal calibrant, generally shows good stoichiometric correlation (without 10%) between H_2 and CO_2 produced and CO consumed.

The duration of any particular run was dictated by the establishment of a relatively stable turnover value (mol gas (mol complex)$^{-1}$ (day)$^{-1}$) over a period of several days and the production of sufficient hydrogen to establish catalytic activity with respect to the metal complex. Notably, with the systems derived from $H_4Ru_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, and $H_2FeRu_3(CO)_{13}$, the reactions were allowed to run sufficiently long to demonstrate catalytic activity with respect to added base.

The hydrogen turnover numbers represent values typically averaged over several recharge cycles stemming from the same experiment. These cycles, with gas sampling occurring immediately prior to flushing, generally extended from approximately 20 to 24 h. The resulting turnover values are normalized to one 24-h (1 day) period. First-day turnover values tended to be significantly different from those of subsequent recharge cycles owing, in general, to maturation of the system to its equilibrium state. (Probably the most significant change during the maturation process is the buffering of the initially strongly alkaline solution by reaction with WGSR product CO_2 and with CO (vide infra)). Therefore, the turnover values reported represent the average activities for the 2 days subsequent to an assumed 24-h induction period and represent values found for duplicate runs or more. A turnover-value (for H_2 production) uncertainty of ±15% is assigned on the basis of uncertainties in the H_2 calibration and in the sampling procedures.

Most systems displayed modest decreases in activity over extended times, generally falling to activities (based on turnover numbers) about half those reported after a period of 8-20 days. Since these decreases occurred for all systems but at varying rates for any individual system, we attribute these to irreversible changes in the catalyst, perhaps reactions with solvent, or with impurities introduced during the periodic flush/recharge cycles. Another possibility is loss of material during the latter manipulations. We are currently exploring this question with the goal of improving catalyst stabilities.

Ruthenium Carbonyls. Variation of the solution composition, in particular the initial concentrations of water or KOH in the exthoxyethanol solvent, had relatively small effects on the catalytic activity of systems prepared from $Ru_3(CO)_{12}$. For example, the activities listed in Table I are for solutions 6 M in H_2O, but turnover numbers found for the ruthenium system gave the same activities within the experimental uncertainties for water concentrations ranging from 1.5 to 6 M. Similarly, with $[H_2O]$ held constant at 6 M, variation of initial [KOH] over the range 0.15-0.6 M had relatively small effects on the solutions' activity over the long term. However, the lower initial [KOH] solutions displayed considerably more activity during the first 24 h of the particular run, but then settled down to similar patterns of behavior. The IR spectra of each of the mature solutions were indistinguishable regardless of the initial [KOH]. Neutral solutions prepared from either $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ in aqueous ethoxyethanol produced modest amounts of H_2 over the first 24 h, but were unstable, with $Ru_3(CO)_{12}$ subliming from the catalyst solutions. Thus, base is indeed necessary to produce the species stable in these solutions. However, high initial concentrations of KOH, 1.9 M, caused decomposition and heterogeneity of the catalyst solution.

The relative insensitivity of these systems' long-term activities to initial [KOH] is not at all surprising given two features of strongly alkaline solutions, namely, the reactions of aqueous hydroxide with both CO_2 and CO (eq 3 and 4) to produce bicarbonate and formate, respectively.

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (3)$$

$$CO + OH^- \rightarrow HCO_2^- \qquad (4)$$

The latter reaction consumes hydroxide with a rate law[27] first order in $[OH^-]$; thus, it is a major process under the conditions initially present in eq 4. Simultaneously, as CO_2 is produced via the shift reaction, it serves also to neutralize hydroxide (eq 3). Accordingly, the pH of catalyst solutions having performed at the reaction temperature for 1 day or longer is found to fall in the range 9.5-10.0, consistent with buffering by the bicarbonate/carbonate equilibrium

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad (5)$$

Potentiometric titration of these matured solutions with HCl indicates that only 10% of the base equivalents are in the carbonate or bicarbonate forms with the remainder as formate. Formate can also be observed in the reaction solutions via IR and NMR spectroscopy.

This leads to the question of whether comparable catalysts can be generated from ruthenium carbonyl utilizing K_2CO_3 or $KHCO_3$ as the initial base. Notably, solutions of $KHCO_3$ in aqueous ethoxyethanol evolve gas when heated to 100 °C presumably according to the equilibrium

$$2HCO_3^- \rightleftharpoons CO_2\uparrow + CO_3^{2-} + H_2O \qquad (6)$$

It is this property which allows CO_2 formation over the catalyst solution. Reaction solutions prepared from $Ru_3(CO)_{12}$ with $KHCO_3/K_2CO_3$ (0.03/0.03 M initial concentration) as the added alkali displayed characteristics (IR spectra and color) as well as catalytic activity identical with those of solutions prepared from KOH as the initial alkali (Table I). When low concentrations of $KHCO_3$ (0.03 M) alone were used with $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$, smaller activities were noted, but comparable, if not greater, activities were seen for much higher initial concentrations of $KHCO_3$ (0.20 M).

Addition of formate as the sodium salt, either initially or to matured solutions, had little effect on the activities of catalysts prepared from $Ru_3(CO)_{12}$ and indeed may have inhibited the mixed metal (Fe/Ru) based systems (vide infra). Our previous report that the ruthenium systems are active for the decomposition of formate ion to H_2 plus CO_2 was based upon an experiment where significant quantities of HCO_2H had been added to the catalyst solution. Similar behavior is also seen for the catalyst prepared from the carbide cluster $Ru_6C(CO)_{17}$ (Table I). The different responses to added sodium formate and formic acid suggest that a lowering of the solution pH is essential to the formate decomposition. This is a subject of our continuing investigation.

Attempts to determine reaction kinetics by monitoring the consumption of CO over a long period (days) without recharging the flask gave uncertain results. Plots of log P_{CO} vs. time for mature alkaline ruthenium carbonyl solutions were initially linear suggesting the reaction to be first order in P_{CO}; however, considerable curvature was evident in the later stages. Linear plots over several half-lives were obtained with the more active mixed Fe/Ru catalysts (vide infra). Nonetheless, in general, the normalized turnover numbers A_{H_2} proved a more reproducible and reliable criterion for examining effects of solution perturbations. The rationale for this lies in the methods of data collection. The A_{H_2} values are determined for short periods (24 h or less) where P_{CO} is essentially constant, diminishing by less than 20% overall; hence, potential errors due to reaction vessel leakage, introduction of air during sampling procedures, etc., are minimized. In addition, possible shifts in P_{CO}-dependent equilibria among the catalyst components during a run are minimized owing to the near constancy of P_{CO}.

Notably, A_{H_2} values at 100 °C appear independent (within experimental uncertainties) of ruthenium concentrations over a sixfold range. For example, three runs under otherwise identical conditions (100 °C, $P_{CO} = 1.0$ atm) with ruthenium concentrations of 0.016, 0.053, and 0.098 g-atom of Ru/L, respectively, gave indistinguishable A_{H_2} values of 1.0 ± 0.2. Given that A_{H_2} is defined as the production of H_2 per day per gram-atom of metal added, this observation allows calculations of the catalysis order in [Ru] as 1.0 ± 0.15. The A_{H_2} values do increase linearly over a fivefold range in initial P_{CO} with A_{H_2} values of 0.45 ± 0.11, 0.95 ± 0.15, and 2.2 ± 0.2 found for a series of solutions (T = 100 °C, [Ru] = 0.051 g-atom/mol) at P_{CO} = 0.42, 0.92, and 2.02 atm, respectively. If one assumes that Henry's law holds for these solutions, the catalysis rate order in dissolved CO is 1.0 ± 0.2. The potential variance of the order in P_{CO} is apparently amplified by the experimental uncertainties resulting from compiling the A_{H2}/P_{CO} dependence from a series of runs for different solutions. When single mature catalyst solutions are considered and P_{CO}(initial) is varied randomly, the activity order in CO is found to be 1.0 with smaller variances (±0.1).

Components in Alkaline Ethoxyethanol of Catalysts Prepared from $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, or $H_2Ru_4(CO)_{13}$. In separate experiments, each of these metal carbonyls under catalytic conditions (see Table I) gives rise to a homogeneous, red-brown solution, exhibiting equivalent normalized catalytic activities A_{H_2} and identical solution IR spectra when examined at ambient temperature. The above indicates the relative ease of interconversion between solution species derived initially from any one of the above neutral ruthenium carbonyls or carbonyl hydrides on the time scale and under the conditions of a catalysis run. Specifically the solution exhibits IR bands on the CO region at 2071 (w), 2037 (s), 2030 (s), 2015 (s), 1998 (s), 1974 (s), and 1952 (s) cm^{-1} (see Figure 1). The ^{1}H NMR spectrum of the ethoxyethanol catalytic solution exhibits two hydride resonances at τ 22.47 and 26.98. The solution is reasonably stable in the presence of air showing no change in its IR spectrum after exposure for 20 min; however, decomposition does take place in a period of hours. Removal of the CO gas phase, followed by vacuum removal of all solvent, followed by readmission of solvent leads to no detectable change in the solution IR spectrum. A legitimate concern, however, is that lowering the solution temperature (100 °C) may lead to major changes in the composition of the species present in the solution. That this is not the case was illustrated by examining the electronic spectra of dilute (~10^{-4} M) aqueous ethoxyethanol solutions prepared from $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ at base compositions comparable to the mature catalyst solutions. After prolonged heating at 100 °C, the solution spectra were recorded at 100 °C, and again, after cooling, at 25 °C. The spectral changes between these conditions were minor, indicating that cooling the solutions does not result in major changes in their compositions.

Vacuum removal of solvent from a catalyst solution prepared from 0.027 g (0.04 mmol) of $Ru_3(CO)_{12}$, 3 mL of 2-ethoxyethanol, 20 mmol of H_2O, and 2 mmol of KOH followed by the addition of $[AsPh_4][Cl]$ in ethanol results in the precipitation of the known, orange-red solid $[AsPh_4][H_3Ru_4(CO)_{12}]$ identified from IR and NMR spectral properties. The IR spectrum of the remaining residue showed the presence of appreciable amounts of the trihydride anion $H_3Ru_4(CO)_{12}^-$, indicating this to be the predominant species in solution as well.

An attempt to separate components of the ruthenium catalyst solution by anion chromatography was unsuccessful. However, separation was sufficient to indicate that the solution contained at least three components: $H_3Ru_4(CO)_{12}^-$, the predominant species, an appreciable percentage of another anionic metal carbonyl (I), and a trace of an orange material not isolated. Species I can be prepared separately and apparently is the trinuclear cluster $HRu_3(CO)_{11}^-$ (vide infra). A synthetic mixture of $[AsPh_4][H_3Ru_4(CO)_{12}]$ and $[NEt_4][HRu_3(CO)_{11}]$ in aqueous ethoxyethanol gives a carbonyl-region IR spectrum analogous to the catalyst solution (bands at 2072, 2037, 2030, 2015, 1998, 1989, 1974, 1952 and 1730 cm^{-1}). Of these, the bands at 2070, 2037, 2030, 2015, 1996 and 1974 cm^{-1} can be attributed to $H_3Ru_4(CO)_{12}^-$ and those at 2072, 2015, 1989, 1952 and 1730 cm^{-1} to I (see Figure 1). Similarly, this synthetic mixture gave two hydride resonances in the ^{1}H NMR spectrum, τ 26.98 ($H_3Ru_4(CO)_{12}^-$) and 22.47 (I), as also seen in the catalyst solution under analogous conditions.

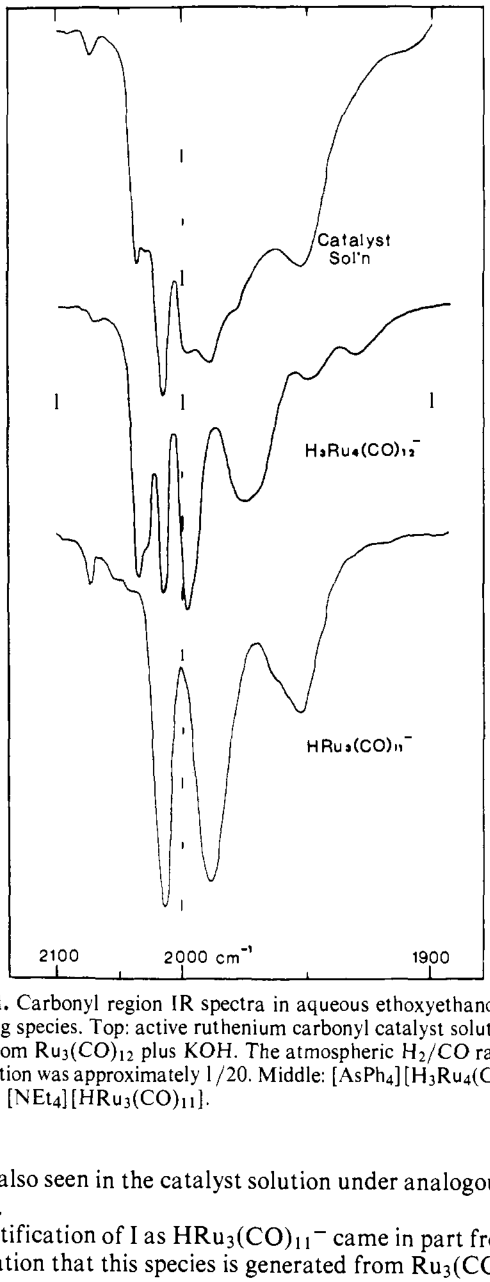


Figure 1. Carbonyl region IR spectra in aqueous ethoxyethanol of the following species. Top: active ruthenium carbonyl catalyst solution prepared from $Ru_3(CO)_{12}$ plus KOH. The atmospheric H_2/CO ratio over this solution was approximately 1/20. Middle: $[AsPh_4][H_3Ru_4(CO)_{12}^-]$. Bottom: $[NEt_4][HRu_3(CO)_{11}]$.

Identification of I as $HRu_3(CO)_{11}^-$ came in part from the observation that this species is generated from $Ru_3(CO)_{12}$ by the room temperature reaction with KOH in aqueous ethoxyethanol (see Experimental Section). The isolated Et_4N^+ salt displays IR and NMR properties close to those described earlier for a preparation[28] of this material of problematical purity and IR and ^{1}H and ^{13}C (low temperature) NMR spectra similar to those of the known iron analogue.[29] The ^{1}H NMR spectrum displays a hydride resonance at τ 22.57 in acetone-d_6 compared to the τ 22.9 reported for $HRu_3(CO)_{11}^-$ (solvent not described).[28] The ^{13}C NMR spectrum in methanol-d_4 at −85 °C exhibits carbonyl carbon resonances at 193.2 (doublet, J = 3.2 Hz), 198.0 (singlet), 203.1 (doublet, J = 13.5 Hz), 208.8 (doublet, J = 5.6 Hz), 209.9 (singlet), 210.6 (singlet), and 281.8 ppm (doublet, J = 5 Hz) with relative intensities of 2:2:2:2:1:1:1, respectively. Raising the temperature to −78 °C had no effect on the ^{13}C NMR spectrum; however, at room temperature the only resonance observed was a very broad band centered at 204.8 ppm indicating the fluxionality of this cluster.

The relative concentrations of $H_3Ru_4(CO)_{12}^-$ and $HRu_3(CO)_{11}^-$ in a typical catalyst solution depend on the composition of the gas phase, the latter ion being favored by low H_2/CO ratios. If this ratio is changed synthetically by flushing and recharging the flask and the solutions are kept at

Table II. WGSR Activities for Fe/Ru Mixtures in Alkaline Aqueous Ethoxyethanol[a]

[Fe][b]	[Ru][c]	[Fe]/[Ru]	base[d]	[base][d]	A_{H_2}[e]
0.012	0.036	0.33	KOH	0.6 M	2.5 ± 0.6
0.018	0.034	0.53	KOH	0.6	4.2
0.028	0.036	0.78	KOH	0.6	7.9
0.060	0.036	1.7	KOH	0.6	5.6
0.43	0.034	12.6	KOH	0.6	1.1
0.012	0.036	0.33	$KHCO_3$	0.03	5.2
0.012	0.036	0.33	$KHCO_3$ K_2CO_3	0.03 0.03	4.7
0.012	0.024[f]	0.50	$KHCO_3$	0.03	4.5

[a] $T = 100$ °C, $P_{CO} = 0.9$ atm. [b] Added to mature Ru catalyst solutions as $Fe(CO)_5$, concentration in g-atoms Fe/L. [c] Initial form $Ru_3(CO)_{12}$, concentrations in g-atoms Ru/L. [d] Form and concentration (M) of base initially added. [e] Normalized activity for H_2 formation in mol H_2 (g-atom total metal)$^{-1}$ (day)$^{-1}$. [f] Initial form $H_4Ru_4(CO)_{12}$.

100 °C, there is a slow but reversible interconversion between the ions. Heating the solution under a H_2 atmosphere for 3 h gave a solution with an IR spectrum in the carbonyl region essentially indistinguishable from that of $H_3Ru_4(CO)_{12}^-$. Flushing and recharging the reaction vessel with CO followed by testing the solution for several hours at 100 °C regenerated a solution IR spectrum analogous to that shown in Figure 1, indicating a mixture of the two anions under conditions where the H_2/CO ratio is small ($P_{tot} \simeq 1$ atm = 5% H_2, ~90% CO, ~5% CO_2). The ^1H NMR spectra of active catalyst solutions confirm this view. For example, the ^1H NMR spectrum of a catalyst solution under an atmospheric P_{H_2}/P_{CO} ratio of about 0.05 displayed two resonances at τ 26.98 ($H_3Ru_4(CO)_{12}^-$) and 22.47 ($HRu_3(CO)_{11}^-$) with the former more intense by a factor of 5, indicating a $H_3Ru_4(CO)_{12}^-/HRu_3(CO)_{11}^-$ ratio of about 5:3.

If a catalyst solution is stirred at 100 °C under a pure H_2 atmosphere for a period of days, there is an irreversible formation of an unidentified species with an intense, broad IR band centered at 1976 cm^{-1}. A similar band is the most prominent feature of the IR spectrum of mature catalyst solutions prepared from the carbide cluster $Ru_6C(CO)_{17}$ in alkaline aqueous ethoxyethanol. Similarly, this band is observed to grow in importance as $Ru_3(CO)_{12}$-based catalysts slowly deactivate over a period of weeks.

Three ruthenium-containing species were identified as the result of neutralizing an active catalyst solution prepared from $Ru_3(CO)_{12}$ (0.16 mmol), KOH (7.3 mmol), and H_2O (100 mmol) in ethoxyethanol (11.2 mL). This solution was quickly cooled to room temperature from the 100 °C operating temperature wherein the gas phase consisted of H_2 (11.9%), CO (81.9%), and CO_2 (6.2%). The IR of the cooled solution indicated $H_3Ru_4(CO)_{12}^-$ to be the major species present. To this mixture, concentrated H_2SO_4 was added dropwise under a nitrogen atmosphere until the solution became nearly colorless owing to precipitation of the ruthenium clusters. The solids were isolated by filtration, washed with water, dried in vacuo, then redissolved in hexane and chromatographed from a silica gel column with hexane as an eluant. The chromatography led to the clean separation of the dihydride $H_2Ru_4(CO)_{13}$ (as a red band) which was identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample.[24] The other component was a yellow-orange band consisting of a $H_4Ru_4(CO)_{12}/Ru_3(CO)_{12}$ mixture (again identified from the IR and ^1H NMR spectra). The quantitative $H_4Ru_4(CO)_{12}/Ru_3(CO)_{12}$ ratio was estimated by comparing the IR spectrum of the experimental mixture with those of $H_4Ru_4(CO)_{12}/Ru_3(CO)_{12}$ mixtures of known composition. Of the ruthenium initially used to prepare the reaction mixture, ~80% was recovered (after elution) as these three species. Of this material, ~75% was $H_4Ru_4(CO)_{12}$, ~15% was $Ru_3(CO)_{12}$, and ~10% was $H_2Ru_4(CO)_{13}$.

Ruthenium catalyst solutions prepared initially from the carbide cluster $Ru_6C(CO)_{17}$ in alkaline ethoxyethanol displayed properties (besides the lower activity) rather different from those of solutions prepared from $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$. The former solutions turned cherry red under catalysis conditions (0.9 atm CO, 100 °C) and subsequently displayed CO-region IR bands at 2034 (w), 2016 (w), 1976 (vs), 1950 (s), 1920 (m), and 1790 (w) cm^{-1}. Acidification of this solution with H_2SO_4 followed by solvent evaporation gave an orange residue with bands at 2082 (w), 2072 (s), 2068 (s), 2060 (s), 2044 (w), and 2024 (w) cm^{-1} (cyclohexane). Neither the solution species under alkaline conditions nor the neutralization product(s) was characterized further; however, it is evident from comparison of IR spectra that neither contained a significant fraction of the original $Ru_6C(CO)_{17}$ (IR bands at 2064 (s), 2049 (s), 2007 (w), 1993 (w), 1958 (w), and 1834 (w) cm^{-1} (cyclohexane)).

Mixed Metal (Fe/Ru) Catalysis. One of the remarkable features of Table I is the observation that the mixed-metal cluster $H_2FeRu_3(CO)_{13}$ is more active than either ruthenium carbonyl or iron carbonyl individually. This synergetic behavior of the mixed-metal system is also observed for catalyst solutions prepared initially from $Ru_3(CO)_{12}$ plus $Fe(CO)_5$ or $Fe_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ plus $Fe(CO)_5$ in alkaline solution (Table II). The catalytic activity of these solutions appears higher when the initial base added is $KHCO_3$ or $KHCO_3$ and K_2CO_3 rather than KOH. Within experimental uncertainties, there appears no distinguishable difference between A_{H_2} values measured when the initial form of the catalyst is the mixed-metal cluster $H_2FeRu_3(CO)_{13}$ or the $Fe(CO)_5/Ru_3(CO)_{12}$ (1:1) mixtures. In addition, IR spectra of the reaction solutions indicate that the nature of the metal carbonyl species present in mature solutions is independent of the form of the initial base added.

The components of these mixed-metal systems were examined as follows. An active ruthenium catalyst solution prepared from 0.15 g (0.23 mmol) of $Ru_3(CO)_{12}$, 12 mL of 2-ethoxyethanol, 0.4 mL of water, and 1.2 mL of 6.6 M KOH (7.90 mmol) was cooled to ambient temperature and 0.08 mL (0.60 mmol) of $Fe(CO)_5$ was added by syringe. The resulting system was reheated at 100 °C, and its activity was verified by GC analysis. The solution IR spectrum consisted of a very weak band at 2072 cm^{-1}, a medium band at 1882 cm^{-1}, a weak band at 1820 cm^{-1}, and a broad, less resolved combination of strong bands at 2036, 2028, 2014, 1994, 1970, and 1952 cm^{-1}. After the solution was cooled to ambient temperature, concentrated sulfuric acid was added dropwise under a nitrogen atmosphere until the initially brown-red solution was almost colorless. The solution was stirred for 30 min; then the solvent was removed by vacuum evaporation. The resulting brown residue was extracted with warm cyclohexane, leaving a very small amount of brown-black residue which was not characterized. The IR spectrum of the filtrate showed bands at 2082, 2073, 2067, 2060, 2056, 2040, 2029, 2023, 2008, 1992, 1884, and 1855 cm^{-1}. Elution on a silica gel column with hexane in a manner previously described for a similar mixture[24] separated the hydrides $H_4Ru_4(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ and lesser amounts of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, and $Ru_3(CO)_{12}$ as identified from their IR spectra. The ^1H NMR spectra confirmed the presence of $H_4Ru_4(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ exhibiting resonances in their respective aliquots at τ 27.73 and 28.54 in $CDCl_3$ as previously reported.[24] A very weak signal at τ 29.0 was also seen. Based on the NMR, IR, and chromatography results, the neutralized mixture had the approximate composition 50% $H_4Ru_4(CO)_{12}$ and 30% $H_2FeRu_3(CO)_{13}$ with the remainder being $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, and $Ru_3(CO)_{12}$. However, this composition is notably short on iron relative to the initial mixture, suggesting loss of iron in the previously noted insoluble residue or by sublimation of $Fe(CO)_5$ from the reaction mixtures on workup.

In a similar experiment with an $Fe(CO)_5/Ru_3(CO)_{12}$ ratio of 5/1, the unacidified solution IR spectrum exhibits an overall shape similar to that in the experiment previously described with discernible IR bands at 2072, 2036, 2029, 2014, 1996, 1970, 1952, 1882, and 1820 cm^{-1}. The ^1H NMR spectrum of residue material under CO in acetone-d_6, resulting from vacuum removal of solvent, indicates the presence of the $H_3Ru_4(CO)_{12}^-$ anion (relative intensity 1) and singlets at τ 18.59 (relative intensity 1) and 25.71 (relative intensity of 0.65). Also observed were two broad resonances of approximately equal intensity at τ 20.79 and 23.19. It was noted that vacuum removal of solvent followed by solvent readmittance produced no change in the catalyst solution IR spectrum.

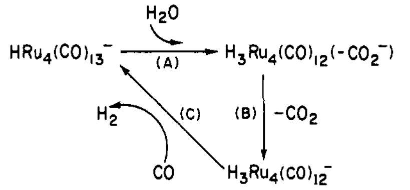
Under similar conditions with KOH as the initial base, $H_2FeRu_3(CO)_{13}$ gives a yellow-brown solution which exhibits IR bands in the CO region at 2071 (w), 2036 (s), 2028 (s), 2014 (s), 1996 (s), 1990 (s), 1970 (s), 1950 (s), and 1882 (m) cm^{-1}. With the exception of the absence of the 1820-cm^{-1} band, seen in the catalytic solutions prepared from $Fe(CO)_5$ and $Ru_3(CO)_{12}$, the overall shape and band frequencies and intensities are similar to those of the latter system. The IR spectrum of the residue resulting from acidification with H_2SO_4 of the catalytic solution confirms the presence of $H_4Ru_4(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$, in comparable quantities, and suggests a mixture of the trimetallic $M_3(CO)_{12}$ species of both homonuclear and heteronuclear varieties.

Discussion

Perhaps the most important feature of Table I, especially when combined with the recent results from other laboratories, is the very broad range of metal complexes and reaction media for which catalysis of the water-gas shift reaction[6-12] has now been recognized. The generality of such catalysis by metal carbonyls in alkaline solution may not be surprising given the long-known reactivity of coordinated CO with nucleophiles, especially hydroxide. More surprising is the activity noted for some complexes in neutral and acidic media,[6,8] although it is now apparent[30] for the ruthenium carbonyls that the natures of the catalytic species are considerably different for the alkaline and acidic solutions.

With regard to potential mechanisms for the shift reaction catalysis in alkaline solution, our discussions will focus largely on the ruthenium carbonyl catalysts. The observations that under relatively mild conditions the rates of catalysis are approximately first order in P_{CO} and in [Ru] have important implications regarding the catalysis cycle. The P_{CO} dependence apparently discredits aspects of Scheme I, since it is unlikely that the rate-limiting step of this scheme would be CO addition to the coordinatively unsaturated species "M". The [Ru] dependence indicates that the nuclearity of the ruthenium species participating in the rate-limiting step is that of the principal ruthenium species in solution (see below). The latter argument assumes sufficient systemic lability so that the various Ru species are present in roughly equilibrium concentrations under the catalysis conditions. This relative lability is indicated by the identical spectral properties of the catalyst solutions independent of whether the ruthenium carbonyl is added originally as $Ru_3(CO)_{12}$, $H_2Ru_4(CO)_{13}$, or $H_4Ru_4(CO)_{12}$. Obviously, this presumed lability does not extend to all the Ru species possible since, under conditions where the partial pressure of H_2 is relatively high, at least one is slowly formed irreversibly.[31,32]

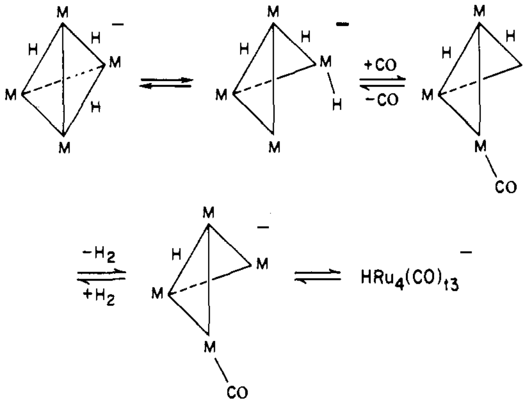
Scheme II



The relatively rapid reactions of ruthenium-coordinated carbonyl with base (as illustrated by the facile synthesis of $HRu_3(CO)_{11}^-$ from $Ru_3(CO)_{12}$ and KOH in ambient aqueous ethoxyethanol) as well as the catalysis rate dependence on P_{CO} imply that CO activation is not rate limiting to the catalysis. The other key step or steps in Scheme I is that of dihydrogen reductive elimination; however, rate-limiting H_2 elimination followed by CO addition is inconsistent with the P_{CO} dependence. Hence, a step involving more direct CO participation in H_2 elimination is indicated, although subtle shifts in the mix of the catalyst components might also lead to an activity dependence on P_{CO}.

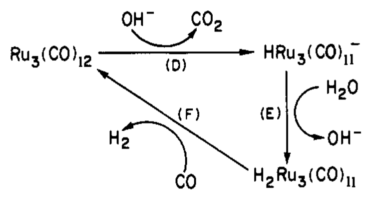
The principal ruthenium species present under the catalysis conditions are the trinuclear anion $HRu_3(CO)_{11}^-$ and the tetranuclear anion $H_3Ru_4(CO)_{12}^-$. The observation of $H_2Ru_4(CO)_{13}$ as a product of catalyst solution neutralization implies the presence of small concentrations of the $HRu_4(CO)_{13}^-$ anion as well, although the dihydride may be the product of other reactions during the neutralization and workup. Nonetheless, the likely presence of both these tetranuclear clusters suggests the operation of a catalytic cycle such as Scheme II. Steps A and B would involve first nucleophilic attack of H_2O on coordinated CO followed by rearrangement and decarboxylation to give the trihydride anion. The rate-limiting process would be C, i.e., CO-assisted H_2 elimination.

Nucleophilic displacements of ligands from both mononuclear[33] and polynuclear[34] metal carbonyls have been observed to occur by second-order rate laws attributed to associative pathways. Also, for at least one case,[35] reductive elimination has been shown to be accelerated by incoming nucleophiles. With polynuclear complexes such as $H_3Ru_4(CO)_{12}^-$, pathways involving scission[34] of a metal-metal bond (e.g., eq 7)

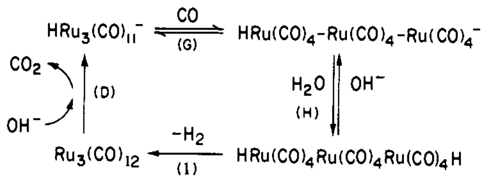


(7)

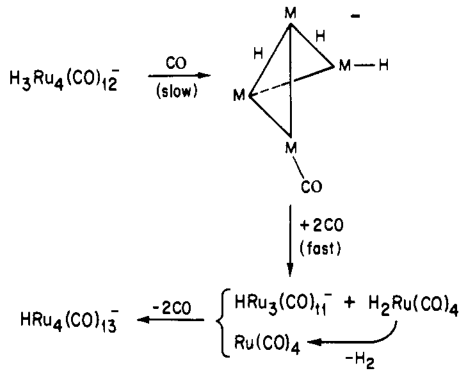
Scheme III



Scheme IV



Scheme V



might also give such second-order rate laws. In such a case, the CO dependence is the result of CO trapping of the "butterfly" structure formed in the initial bond scission, competitive with reclosure to the $H_3Ru_4(CO)_{12}^-$ tetrahedron.

An analogous cycle can be proposed for trinuclear species, e.g., Scheme III. The feasibility of Scheme III has been demonstrated in individual steps. The trinuclear cluster reacts rapidly in alkaline ethoxyethanol to form $HRu_3(CO)_{11}^-$ (see Experimental Section) while acidification of $HRu_3(CO)_{11}^-$ under a CO atmosphere leads to formation of $Ru_3(CO)_{12}$.[36] Although it has been reported[37] that prolonged exposure of the osmium analogue $H_2Os_3(CO)_{11}$ to CO leads to $Os_3(CO)_{12}$, the kinetics for this reaction have not been described. Again what role CO would have in the H_2 elimination step F is unclear. Shriver has noted the very low basicity of the iron analogue $HFe_3(CO)_{11}^-$ and that the site of protonation is the oxygen of a bridging carbonyl.[29b] Similarly we have found that an excess of strong acid H_2SO_4 is necessary for the facile conversion of $HRu_3(CO)_{11}^-$ to $Ru_3(CO)_{12}$.[36] Thus one might speculate that H_2 elimination in alkaline solution requires a different sequence of steps than E and F, e.g., Scheme IV. The key here would be the enhanced basicity of the open-chain anion, $H[Ru(CO)_4]_3^-$. The osmium analogue of the open-chain dihydride $H_2[Os(CO)_4]_3$ has been characterized and found to be relatively stable, although thermolysis at 160 °C gives the triangular cluster $Os_3(CO)_{12}$ in analogy to step I.[38] The open-chain triruthenium dihydride $H_2[Ru(CO)_4]_3$ has been previously proposed[39] as the relatively unstable product of the decomposition of $H_2Ru(CO)_4$.

It is conceivable that catalysis of the shift reaction might be occurring by mechanisms involving both tetra- and trinuclear clusters. The relative independence of the normalized activities to ruthenium concentration may simply reflect similar rates for the two cycles. However, even if one of these cycles were dominant, kinetic order near unit is predicted for ruthenium (i.e., A_{H_2} should have little ruthenium dependence) and the present data may not be able to differentiate this behavior.[40] The observation of fairly labile interconversion between the two predominant species $HRu_3(CO)_{11}^-$ and $H_3Ru_4(CO)_{12}^-$ suggests one other cycle involving such a change in nuclearity and which may lead to H_2 elimination (Scheme V). A somewhat similar mechanism for H_2 elimination via a declusterification step has been suggested by Geoffroy.[41] Notably, the last scheme ties together Schemes II and III and one cannot discriminate against the possible simultaneous operation of all these cylces. We are presently examining the molecular dynamics of the various interconversions with the goal of elucidating the relevant mechanisms.

The synergetic catalysis by the mixed metal (Fe/Ru) carbonyl system is consistent with catalytic cycles in which the rate-limiting path is reductive elimination of H_2 from a cluster hydride species. The mixed tetranuclear cluster $H_4Ru_3Fe(CO)_{12}$ has been reported as considerably less stable than the $H_4Ru_4(CO)_{12}$ homologue toward loss of H_2.[23] Any of the H_2 elimination steps of the proposed cycles of the preceding discussion may be more rapid with mixed-metal clusters such as those found in the Fe-Ru catalyst systems. Again, this is an area of continuing exploration in these laboratories.

In summary, for the ruthenium carbonyl catalysis of the shift reaction, our evidence points to the catalytic cycles involving polynuclear ruthenium clusters as the probable catalysts and to CO-assisted H_2 elimination as the rate-limiting step (or steps) for the kinetically important cycles. The synergetic behavior of the mixed metal (Fe/Ru) catalysts is consistent with such a scheme; however, the specifics of such catalytic cycles are largely in the speculative stage of development at present. Although clusters are the possible active species in the alkaline ruthenium carbonyl catalysts, it is apparent from recent studies involving other metal carbonyl complexes[6,10-12] that the presence of metal clusters is not a prerequisite for shift reaction homogeneous catalysis.

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(31) A likely candidate for this species is the anionic carbide complex $Ru_6C(CO)_{16}{}^{2-}$ since its IR spectrum is consistent with that of the reaction product of KOH plus $Ru_6C(CO)_{17}$ in aqueous ethoxyethanol (2034 w, 2016 w, 1976 vs, 1950 sh, s, 1920 w, 1790 w cm^{-1}). The latter spectrum is reminiscent of the IR spectrum of the iron species $Fe_6C(CO)_{16}{}^{2-}$ (1964 s, 1957 sh, 1930 sh, 1775 w cm^{-1}).[33]

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(40) For example, if trinuclear Ru_3 cluster were solely responsible for the catalysis yet the vast majority of ruthenium were present in Ru_4 clusters and a labile $4Ru_3 \rightleftarrows 3Ru_4$ equilibrium were extant under catalysis conditions, then the kinetic order in $[Ru_{total}]$ would be 0.75. The reverse case would give an order of 1.33. The presence of significant equilibrium concentrations of both types of clusters (as seen in the present case) would give an apparent order between these two limits as would be the case when both types of clusters have comparable activities for the shift reaction. Given that the range of activities noted for WGSR catalysis by various group 8 metal carbonyls is relatively narrow, it certainly does not seem unreasonable that clusters of the same metal but of different nuclearities would have comparable reactivities.

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Autoxidation of Transition-Metal Complexes. Reaction of a 1:1 Cobalt–Molecular Oxygen Complex with Acids to Yield Hydrogen Peroxide. Kinetics and Mechanism

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Abstract: Dioxygen (pyridine)-*N,N'*-ethylenebis(acetylacetoniminato)cobalt(II) reacts with acids in organic solvents containing excess pyridine to give 0.5 mol of molecular oxygen, 0.5 mol of hydrogen peroxide, and 1 mol of dipyridine *N,N'*-ethylenebis(acetylacetoniminato)cobalt(III) ion as an ion pair with the anion of the acid. In pyridine below 0 °C the reaction proceeds quantitatively within experimental uncertainty, and no detectable buildup of intermediates is observed. Kinetic studies were done with acetic acid in pyridine at −10.7 °C by monitoring the evolution of oxygen at constant pressure. The empirical rate law is found to be second order in the cobalt oxygen complex, inverse first order in oxygen pressure, inverse one-half order in cobalt(III) acetate product, and between second and third order in acetic acid. This law holds throughout the course of the reaction, strongly indicating that only one mechanism is in operation. The effect of added bromide and acetate salts on the rate and the demonstrated occurrence of the homoconjugation equilibrium for acetate, $OAc^- + HOAc \rightleftarrows H(OAc)_2{}^-$, lead to the conclusion that the high empirical order in acetic acid is equivalent to a first-order dependence each on acetic acid and free, dissociated pyridinium ion. The proposed mechanism involves protonation, and subsequent dissociation as hydrogen peroxide, of the bridging dioxygen ligand from a binuclear complex intermediate, $pyCo(acacen)O_2Co(acacen)py$, which exists in rapid equilibrium with the starting mononuclear dioxygen complex. The involvement of both acid species in the transition state is discussed. The absence of free-radical intermediates was strongly indicated by the results of experiments carried out in the presence of organic radical scavengers and by ESR spectroscopy. The reaction is discussed in terms of autoxidation of transition-metal complexes.

Introduction

Autoxidation reactions of transition-metal complexes are represented by the equation

$$2M + O_2 \xrightarrow{2H^+} 2M^+ + H_2O_2 \xrightarrow[2H^+]{2M} 2M^+ + 2H_2O \quad (1)$$

where M represents the ligated metal in the reduced state. The initial product, hydrogen peroxide, is usually not observed because it rapidly oxidizes two more metal ions. Most of the investigative work into mechanism has been done on first-row transition metals: Ti(III), V(II, III, IV), Cr(II), Mn(II), and most frequently Fe(II), Co(II), and Cu(I). The mechanisms that have been invoked for the production of hydrogen peroxide in the first step fall into two categories. In eq 2 dissociation of an initial oxygen adduct of the metal complex into oxidized metal and superoxide ion or the hydroperoxyl radical (pK_a of $HO_2\cdot$ is 4.88[1]) occurs which is then followed by fast oxidation of another metal complex by $O_2{}^-\cdot$ $(HO_2\cdot)$.[2-5] Evidence other than kinetics for this scheme is lacking; in particular the species

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