

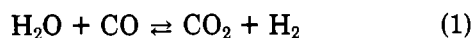
## The Water Gas Shift Reaction: Homogeneous Catalysis by Ruthenium and Other Metal Carbonyls

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The past several years have seen a rekindling of interest in the catalysis chemistry of a classic reaction, the water gas shift reaction (WGSR, eq 1). The current



attention derives naturally from the perceived necessity to produce gaseous and liquid hydrocarbon fuels and other organic chemicals from nonpetroleum sources (e.g., coal). Virtually all schemes for such purposes require copious quantities of hydrogen for conversion of hydrogen-deficient substrates to hydrocarbons or of synthesis gas for Fischer-Tropsch type syntheses. However, the major source of hydrogen now commercially produced is from the steam re-forming or partial oxidation of hydrocarbons, and a different source is an obvious requirement. One such source is in fact an old one: High-temperature reaction of carbonaceous materials with water, normally carried out with the partial oxidation of the substrate, produces mixtures of gases:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{CO}$ , i.e., "water gas". Via the shift reaction, the composition of the mixture can be adjusted to give (after  $\text{CO}_2$  and  $\text{H}_2\text{O}$  removal) hydrogen for the application noted above (or others such as ammonia manufacture) or synthesis gas with the various  $\text{H}_2/\text{CO}$  ratios appropriate to the production of methane, methanol, higher hydrocarbons or alcohols, etc.

Commercially, the shift reaction is carried out over solid metal oxide catalysts at elevated temperatures.<sup>1</sup> The most common is a type based on  $\text{Fe}_3\text{O}_4$  promoted by  $\text{Cr}_2\text{O}_3$  which operates at about 350 °C, but a more active catalyst is one based on copper with zinc oxide. The latter operates at lower temperatures but is considerably more susceptible to sulfur poisoning. Another low temperature catalyst based on  $\text{K}_2\text{CO}_3$ ,  $\text{CoO}$ , and  $\text{MoO}_3$  on alumina has been recently developed by Exxon.<sup>1b</sup> Thus there is continued interest in developing effective low-temperature catalysts given the lower

thermal input requirements and the greater reaction efficiencies indicated by the WGSR thermodynamics for such conditions.<sup>2</sup>

Our interests in this area was stimulated a few years ago when Professor R. G. Rinker, a UCSB colleague in the Chemical Engineering Department, asked for advice regarding homogeneous catalysts for the shift reaction. His aim was to employ such catalyst in a "supported liquid phase reactor", a device where chemical processes can be carried out in a flow reactor configuration with homogeneous catalysts immobilized by dissolving in an involatile solvent supported on a solid substrate. The requested advice was the stimulus for a collaboration which resulted in the discovery of a ruthenium-based WGSR homogeneous catalyst first reported in early 1977<sup>3</sup> and for a longer term effort to develop such catalysts and to elucidate the fundamental reaction mechanisms involved. As often happens, interest in this topic also developed simultaneously in at least two other academic research groups (those of Richard Eisenberg and of Rowland Pettit), and subsequent to the independent reports<sup>3-5</sup> of homogeneous shift reaction catalysts from the three groups in 1977, there have been significant new contributions from others in this lively area of inquiry.<sup>6</sup>

(1) (a) C. L. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, New York, 1970, p 104; (b) C. L. Aldrige, U.S. Patent 3580840 (1974).

(2) Thermodynamic parameters for eq 1 at 298 K are  $\Delta G^\circ = -6.82$  kcal/mol,  $\Delta H^\circ = -9.84$  kcal/mol,  $\Delta S^\circ = -10.1$  eu for  $\text{H}_2\text{O}(\text{g})$ ;  $\Delta G^\circ = -4.76$  kcal/mol,  $\Delta H^\circ = 0.68$  kcal/mol,  $\Delta S^\circ = +18.3$  eu for  $\text{H}_2\text{O}(\text{l})$ .

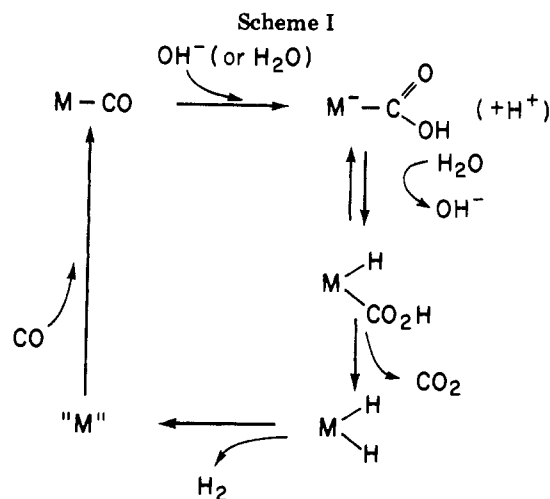
(3) R. M. Laine, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977).

(4) C. H. Cheng, D. E. Hendriksen, and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 2791 (1977).

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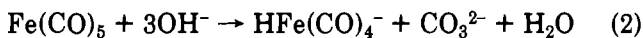
(6) (a) R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, *J. Am. Chem. Soc.*, **100**, 2925 (1978); (b) C. H. Cheng and R. Eisenberg, *ibid.*, **100**, 5968 (1978); (c) T. Yoshida, Y. Ueda, and S. Otsuka, *ibid.*, **100**, 3941 (1978); (d) C. C. Frazier, R. Hanes, A. D. King, and R. R. King, *Adv. Chem. Ser.*, No. 173, 94 (1979); (e) D. J. Darensbourg, M. Y. Darensbourg, R. R. Burch, J. A. Froelich, and M. J. Incorvia, *ibid.*, No. 173, 106 (1979); (f) R. Pettit, K. Cann, T. Cole, C. H. Mauldin, and W. Slegier, *ibid.*, No. 173, 121 (1979); (g) R. G. Nuzzo, D. Feitler, and G. M. Whitesides, *J. Am. Chem. Soc.*, **101**, 3683 (1979); (h) T. C. Singleton, L. J. Park, J. C. Price, and D. Forster, *Prepr. Div. Pet. Chem., Am. Chem. Soc.*, **24**, 329 (1979); (i) R. C. Ryan, G. M. Wileman, M. P. Dalsarets, and C. U. Pittman, *J. Mol. Catal.*, **5**, 319 (1979); (j) R. M. Laine, *J. Am. Chem. Soc.*, **100**, 6451 (1978); (k) E. C. Baker, D. E. Hendriksen, and R. Eisenberg, *ibid.*, **102**, 1020 (1980); (l) A. D. King, R. B. King, and D. B. Yang, *ibid.*, **102**, 1028 (1980).

Peter C. Ford was born in California in 1941. His undergraduate work at Caltech was followed by graduate work at Yale University, where he received his Ph.D. degree with Kenneth B. Wiberg in 1966. After a year as an NSF postdoctoral fellow at Stanford University with Henry Taube, he joined the Department of Chemistry, University of California, Santa Barbara, where he is now Professor. In 1971, he was awarded a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant. Dr. Ford's research interests have been directed toward two general areas, the mechanistic photochemistry of transition-metal complexes and the reactions and properties of coordinated ligands.



### A Model for Catalysis

Initial studies in this laboratory drew inspiration from the early work of Hieber and subsequent researchers<sup>7</sup> who demonstrated that metal carbonyls underwent reactions with aqueous bases to give metal carbonyl anions (or metal carbonyl hydride anions, e.g., eq 2).



Acidification of these solutions released both  $\text{H}_2$  and  $\text{CO}_2$ , the latter product from the neutralization of carbonate, the former presumably from protonation of the metal carbonyl anions to give metal hydrides (e.g.,  $\text{H}_2\text{Fe}(\text{CO})_4$ ) which undergo reductive elimination of  $\text{H}_2$ . While the sum of these procedures obviously requires the stoichiometric consumption first of base, then of acid, it does lead to the WGSR products. Consequently, we postulated that under moderately alkaline conditions, the shift reaction might proceed catalytically according to a hypothetical cycle such as illustrated in Scheme I.

This cycle consists of four key steps: (a) nucleophilic attack of hydroxide (or water) on coordinated CO to give the hydroxycarbonyl intermediate, (b) decarboxylation to give the metal hydride or corresponding anion, (c) reductive elimination of  $\text{H}_2$  from the hydride, and (d) coordination of new CO. In addition there are several potentially crucial protonation/deprotonation equilibria involving metal hydrides or the hydroxycarbonyl. Notably, prior to our catalysis studies there was ample precedent to establish the potential viability of each step, including the formation of hydroxycarbonyl complexes.<sup>8</sup>

### Reactions in Alkaline Solution

In the context of the proposed model, a number of metal carbonyls including both mononuclear and cluster complexes were screened for their potential activity in

alkaline solution. One of our guiding principles was that the simplest systems, i.e., simple metal carbonyls  $\text{M}_x(\text{CO})_y$  and aqueous solution, would be the most utilitarian. However, this rule was quickly bent when it was decided to employ mixed aqueous organic solvents in order to have higher solubilities both of CO and of the metal carbonyls. One of the first metal carbonyls which was examined and the first system we were confident to be truly catalytic in metal and in base for the WGSR is the ruthenium carbonyl system described in greater detail below. However, it is particularly notable that a number of the simple transition-metal carbonyls  $\text{M}_x(\text{CO})_y$  in alkaline solution (or solutions to which organic amines had been added) are precursors to active WGSR catalysts. These include the carbonyls of iridium, iron, osmium, rhodium, rhenium, platinum, molybdenum, tungsten, and chromium.<sup>3,4d,9-11</sup> In addition, more complicated systems with additional ligands such as pyridines,<sup>9</sup> cyclopentadienyl,<sup>9</sup> and phosphines<sup>9,6c</sup> as well as mixed metal carbonyls<sup>10</sup> have shown catalytic behavior under these conditions. Thus, one can conclude that the ability to form such shift reaction catalysts is a quite general reactivity property of metal carbonyl in basic solutions containing water.

Mechanistic studies of the WGSR catalysis in basic solutions are limited; the only published-in-depth studies of the simple carbonyls (and these are certainly incomplete) are of the system using  $\text{Fe}(\text{CO})_5$  and  $\text{Ru}_3(\text{CO})_{12}$  as the catalysts precursors. In a recent report King and co-workers<sup>6e</sup> studied the WGSR by iron carbonyl in alkaline aqueous methanol over the temperature and  $P_{\text{CO}}$  ranges 130–180 °C and 10–40 atm in stainless steel autoclaves. Under these conditions, the system appeared rather simple: in situ infrared studies indicated the presence of only the mononuclear species  $\text{Fe}(\text{CO})_5$  and  $\text{HFe}(\text{CO})_4^-$ , and rate studies showed  $\text{H}_2$  production to be independent of  $P_{\text{CO}}$ . Thus, it was concluded that the WGSR mechanism in this case is strictly analogous to Scheme I ( $\text{M} = \text{Fe}(\text{CO})_4$ ). Given the tendency of the system to be less active at lower pH's, the rate-limiting step was presumed to be the activation of coordinated CO by nucleophilic attack by  $\text{OH}^-$  (eq 2).

Under somewhat different conditions, the ruthenium-based system has proved considerably more intricate. This was examined in some detail in our laboratories at lower temperatures (90–120 °C) and lower pressures ( $P_{\text{CO}} = 0.5\text{--}2.0$  atm) in all-glass reactors with alkaline aqueous ethoxyethanol as the solvent.<sup>12</sup> Solutions prepared initially from  $\text{Ru}_3(\text{CO})_{12}$  with KOH as the base underwent transformations both of the metallic species and of the base during the first few hours before maturation to an equilibrium state. Mature solutions maintained approximately constant catalytic activity (approximately three turnovers/day per mol of  $\text{Ru}_3(\text{CO})_{12}$  added initially at  $T = 100$  °C and  $P_{\text{CO}} = 1$

(7) (a) W. Hieber and F. Leutert, *Z. Anorg. Allg. Chem.*, **204**, 145 (1932); (b) J. W. Reppe, *Liebigs Ann. Chem.*, **583**, 121 (1953); (c) N. S. Imanitov, B. E. Kuvaev, and D. M. Rudkovskii, *Zh. Prikl. Khim.*, **40**, 2831 (1967); (d) D. M. Fenton, U.S. Patents 3490872 and 3539298 (1970); (e) H. W. Sternberg, R. Markly, and I. Wender, *J. Am. Chem. Soc.*, **79**, 6116 (1957); (f) H. Hohenschutz, N. von Kutepow, and W. Himmele, *Hydrocarbon Process.*, **45**, 141 (1966); (g) H. C. Clark, and W. J. Jacobs, *Inorg. Chem.*, **9**, 1229 (1970).

(8) (a) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 443, (1969); (b) J. E. Bercaw, Z.-Y. Gok, and J. Halpern, *J. Am. Chem. Soc.*, **94**, 6534 (1972); (c) T. G. Appleton and M. A. Bennett, *J. Organomet. Chem.*, **55**, C88 (1973); (d) M. Rossi and A. Sacco, *J. Chem. Soc., Chem. Commun.*, 471 (1969); (e) E. L. Muetterties, *Inorg. Chem.*, **4**, 1841 (1965).

(9) S. A. Moya, M. A. Dissertation, University of California, Santa Barbara, 1979.

(10) P. C. Ford, R. G. Rinker, C. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, *J. Am. Chem. Soc.*, **100**, 4595 (1978).

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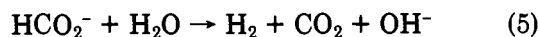
(12) C. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **101**, 5922 (1979).

atm) for a number of days and demonstrated good stoichiometry with regard to CO consumption vs. CO<sub>2</sub> and H<sub>2</sub> production. Solutions were run for sufficient time with periodic flushing and recharging of the reactant gases to demonstrate several hundred turnovers with respect to the ruthenium present and unequivocal catalysis with respect to added base. In addition, reactions run with D<sub>2</sub>O as one substrate gave HD/D<sub>2</sub> product ratios appropriate to water or water exchangeable protons being the dihydrogen source. Lastly the catalytic activities were unaffected by small quantities of added H<sub>2</sub>S.<sup>11b</sup>

The maturation process is accompanied by marked changes in the solution pH owing to the reaction of hydroxide with both the substrate CO and the WGSR product CO<sub>2</sub> to give formate and bicarbonate, respectively (eq 3 and 4). The result is the buffering of the



reaction solution to pH ~9.5 consistent with a bicarbonate/carbonate equilibrium, but only 10% of the base equivalents were present as HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup>, the remainder being formate. (Similar observations have been made for the catalyst based on Fe(CO)<sub>5</sub>, and, given the relative ease by which CO reacts to give HCO<sub>2</sub><sup>-</sup> in strongly alkaline solutions, this reaction must be a complication in many systems.) Notably, catalyst solutions prepared from Ru<sub>3</sub>(CO)<sub>12</sub> with KHCO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> as the added alkali displayed spectral characteristics and catalytic activity identical with those prepared with KOH, and formate, added as NaHCO<sub>2</sub>, had little effect on the catalytic activity. This last point is important given a possible alternative scheme<sup>11</sup> for the WGSR, namely, reaction of CO with base to give formate (eq 3) followed by catalytic decomposition of that substrate (eq 5). Although this mechanism apparently is not



dominant for either the iron- or ruthenium-based homogeneous catalysts, it certainly cannot be universally eliminated from consideration. Indeed an analogous mechanism is proposed for heterogeneous WGSR catalysis,<sup>1</sup> and preliminary results from this laboratory suggest that formate decomposition plays an important role in the homogeneous WGSR by alkaline iridium carbonyl.

The mature reaction solutions contain a mixture of trinuclear and tetranuclear ruthenium clusters: H-Ru<sub>3</sub>(CO)<sub>11</sub><sup>-</sup>, H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>, Ru<sub>3</sub>(CO)<sub>12</sub>, and a fourth species, probably the HRu<sub>4</sub>(CO)<sub>13</sub><sup>-</sup> cluster anion. The first two constitute most of the ruthenium in solution, but when the H<sub>2</sub>/CO ratio is 0.05 or greater, the H<sub>3</sub>-Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup> anion is predominant. The composition of the reaction solutions and the catalytic activities are independent of whether the ruthenium source for the catalyst solution is Ru<sub>3</sub>(CO)<sub>12</sub>, H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub>, or H<sub>4</sub>-Ru<sub>4</sub>(CO)<sub>12</sub>. Thus, under the reaction conditions under which these solutions proved active, it is apparent that the relative ruthenium clusters are sufficiently labile to interconvert one to another.

Kinetics studies of the ruthenium system show the rates of H<sub>2</sub> production to be first order (actually 1.00 ± 0.15) in [Ru]<sub>total</sub> over the range 0.016 to 0.098 mol of Ru/L and first order (1.0 ± 0.1) in P<sub>CO</sub> over the range

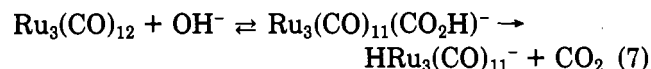
0.4 to 2.0 atm.<sup>12</sup> The apparent activation energy is ~25 kcal/mol. The first-order dependence on ruthenium concentration has some interesting implications with regard to the nuclearity of the active species in the catalytic cycle. Given the considerable lability between the various ruthenium carbonyl complexes under the reaction conditions, the first-order behavior implies that the nuclearity of the ruthenium in the rate-determining step is the same as that of the principal species in solution. However there are two such species, the tetranuclear H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup> and the trinuclear HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup>, the former generally the more prominent under the reaction conditions. Thus under these circumstances, significant contribution to the overall catalysis by mononuclear species is unlikely, but differentiation between catalytic cycles utilizing either trinuclear or tetranuclear species cannot be made based on the kinetic results. In fact, given the activities of various metal carbonyls toward the shift reaction, it would seem unwise to presume that a single catalytic cycle is operable in a complex system such as this.

The first-order kinetics dependence on P<sub>CO</sub> contrasts with the behavior described above for the Fe(CO)<sub>5</sub> based catalyst<sup>6e</sup> and with that expected for the Scheme I. In Scheme I the only role of free CO would be to react with the coordinatively unsaturated "M", a step that is unlikely to be rate determining. Thus CO must be involved in another key step of the cycle, a logical choice being direct participation in the reductive elimination of H<sub>2</sub>, e.g.,



Reductive elimination as the rate-limiting step is consistent with the predominant clusters in solution being the reduced (and hydrogen rich) ruthenium species HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> and H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>.

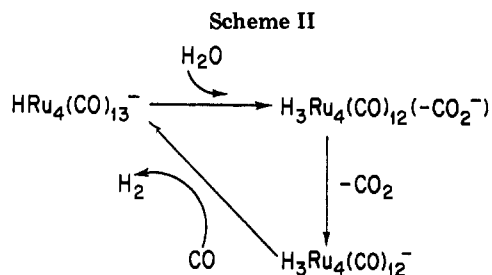
In this context, we have proposed two catalytic cycles, one based on trinuclear clusters, the other upon tetranuclear clusters, the mechanistic details of which are currently under experimental scrutiny. For the trinuclear species, activation of CO by the reaction of OH<sup>-</sup> with Ru<sub>3</sub>(CO)<sub>12</sub> (eq 7) is quite facile. In tetrahydrofuran



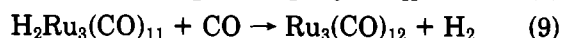
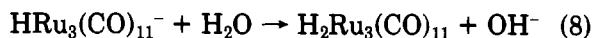
solution, the reaction between Ru<sub>3</sub>(CO)<sub>12</sub> and OH<sup>-</sup> to form an intermediate (believed to be the hydroxycarbonyl cluster) is rapid even at room temperature. Subsequent decarboxylation to give HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> occurs more slowly but is too rapid to be rate determining under the more strenuous catalysis conditions. Notably, Ru<sub>3</sub>(CO)<sub>12</sub> also reacts very rapidly with CH<sub>3</sub>O<sup>-</sup> in deaerated methanol (*k* = 1.5 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> at 25 °C) to form an adduct spectrally very similar to the proposed hydroxycarbonyl intermediate. This reaction is apparently reversible with an equilibrium constant of ~500 M<sup>-1</sup>. In anhydrous solution the methoxy adduct is indefinitely stable, but reacts within minutes to give HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> when water is added.<sup>13</sup>

At room temperature the HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> product of eq 7 is quite stable. However, addition of acid to the reaction solution under a CO blanket leads to the quantitative formation of Ru<sub>3</sub>(CO)<sub>12</sub>, plus H<sub>2</sub> and CO<sub>2</sub>,

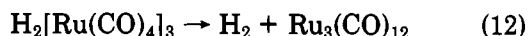
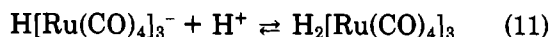
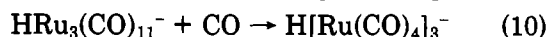
(13) D. C. Gross and P. C. Ford, reported at the 2nd North American Chemical Congress, Las Vegas, NV, August 1980.



stoichiometrically,<sup>12,13</sup> giving a cluster analogy to the iron carbonyl reactions reported by Hieber<sup>7a</sup> (vide supra). In this context, one might propose that the trinuclear cycle may be closed by successive protonation and CO-assisted H<sub>2</sub> elimination (eq 8 and 9). However,



HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> is an exceedingly weak base,<sup>14</sup> leading one to question whether eq 8 can be viewed as a realistic step in the catalysis cycle in alkaline solution. Alternatively, the sequential protonation and carbonylation could be reversed (eq 10–12) to give an open-chain



species H[Ru(CO)<sub>4</sub>]<sub>3</sub><sup>-</sup>. The advantage of this sequence is that the open-chain anion, having a terminal protonation site, should be considerably more basic than the closed triangular cluster HRu<sub>3</sub>(CO)<sub>11</sub><sup>-</sup> where the protonation site is on the oxygen of a bridging carbonyl.<sup>14,15</sup> While the open-chain triruthenium species H<sub>2</sub>[Ru(CO)<sub>4</sub>]<sub>3</sub> and H[Ru(CO)<sub>4</sub>]<sub>3</sub><sup>-</sup> are as yet unknown,<sup>16,17</sup> the osmium homologue H<sub>2</sub>[Os(CO)<sub>4</sub>]<sub>3</sub> has been well characterized and does undergo reactions analogous to eq 11 and 12. For examples, we have shown the pK<sub>a</sub> of H<sub>2</sub>[Os(CO)<sub>4</sub>]<sub>3</sub> in methanol to be 14.7,<sup>18</sup> indicating that the corresponding anion is quite basic, and the osmium analogue to eq 12 was seen in the solid-state thermolysis of H<sub>2</sub>[Os(CO)<sub>4</sub>]<sub>3</sub> at 120 °C to give Os<sub>3</sub>(CO)<sub>12</sub> and other products.<sup>19</sup> Given that the osmium carbonyl hydrides tend to be more robust than the ruthenium homologues, eq 12 should be facile under the catalysis conditions.

Scheme II outlines a catalytic cycle based upon the tetranuclear clusters. Again the rate-limiting step is viewed as CO-assisted H<sub>2</sub> elimination, in this case from H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>, the predominant ruthenium species in the active catalyst solution. Alternatively, H<sub>2</sub> elimination might occur from the conjugate acid H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> since the anion is sufficiently basic (pK<sub>a</sub> = 11.9 in anhydrous methanol)<sup>20</sup> that the solutions will contain

(14) H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem. Soc.*, **100**, 5239 (1978).

(15) J. B. Keister, *J. Organometal. Chem.*, **190**, C43 (1980).

(16) Stone and co-workers<sup>17</sup> have reported an unstable species which they suggest to be H<sub>2</sub>Ru<sub>3</sub>(CO)<sub>12</sub> as a decomposition product of H<sub>2</sub>Ru(CO)<sub>4</sub>.

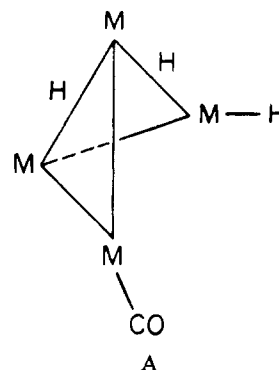
(17) J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 2162 (1968).

(18) H. W. Walker, R. G. Pearson, and P. C. Ford, Abstracts, 179th National Meeting of the American Chemical Society Houston, TX, INOR-159.

(19) J. R. Moss and W. A. G. Graham, *J. Chem. Soc., Dalton Trans.*, 89 (1977).

(20) H. W. Walker, C. Kresge, P. C. Ford, and R. G. Pearson, *J. Am. Chem. Soc.*, **101**, 7428 (1979).

small concentrations of the tetrahydride. Regardless, some precedence exists both for the nucleophilic displacement of ligands from mononuclear and polynuclear metals carbonyls by associative pathways<sup>21</sup> and for reductive elimination accelerated by incoming CO.<sup>22</sup> Such associative pathways might involve a simple concerted displacement, but another possible pathway would be the initial transformation of the tetrahedral cluster via initial scission of a metal–metal bond to a butterfly structure such as A (M = Ru(CO)<sub>3</sub>).



An especially interesting observation we have made is that mixed iron/ruthenium carbonyl catalysts in alkaline or amine solutions are more active than catalysts prepared analogously from either iron or ruthenium carbonyl individually. Characterization of the reaction solutions again demonstrated the presence of both tetranuclear and trinuclear clusters; notably, significant components of each type are mixed-metal clusters. The synergetic behavior of these mixed iron/ruthenium carbonyl systems is consistent with catalytic cycles such as Scheme II in which the slow step is H<sub>2</sub> reductive elimination from a cluster hydride. For example, the mixed tetranuclear cluster H<sub>4</sub>Ru<sub>3</sub>Fe(CO)<sub>12</sub> is reportedly much less stable than the H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> homologue toward loss of H<sub>2</sub>.<sup>23</sup> One might speculate that this enhanced reactivity is due to greater lability of the metal–metal bonds in the mixed-metal cluster. However, another difference is that the mixed cluster H<sub>3</sub>Ru<sub>3</sub>Fe(CO)<sub>12</sub><sup>-</sup> is about two orders of magnitude more basic<sup>20</sup> than H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>, suggesting that a pathway requiring protonation to the tetrahydride prior to reductive elimination would also be more favorable in the former case. Interestingly, small quantities of H<sub>2</sub>S in the feed stream rapidly deactivate the iron in the catalysis solution by precipitating this component but leave behind a ruthenium solution with an activity comparable to a similar catalyst solution prepared from ruthenium alone at that concentration.<sup>11b,24</sup>

### Reactions in Acidic Solutions

While two of the 1977 reports of WGS homogeneous catalysts (ours<sup>3</sup> and Pettit's<sup>15</sup>) were concerned with metal carbonyls in basic solutions, the third (Eisenberg's<sup>4</sup>) utilized a strongly acidic reaction medium. In acid the CO must be sufficiently activated by coordination to be susceptible to nucleophilic attack by water

(21) (a) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967);

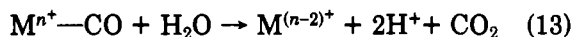
(b) A. Poe and M. V. Twigg, *Inorg. Chem.*, **13**, 2582 (1974).

(22) D. R. McAlister, D. K. Erwin, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 5967 (1978).

(23) S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).

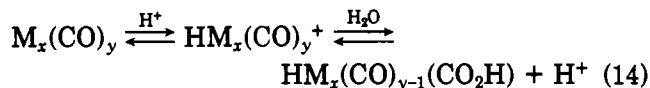
(24) V. Landis and P. C. Ford, unpublished results.

rather than hydroxide. Such might be the case when the metal is in a high oxidation state given that one stage of the metal-catalyzed reaction of CO with H<sub>2</sub>O can be represented as the formal two-electron reduction of the metal center (eq 13). In such a case, oxidation

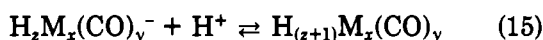


states are somewhat ambiguous given that the conjugate acid of M<sup>(n-2)+</sup> is MH<sub>2</sub><sup>n+</sup> and that formal representation of coordinated hydrogen as a hydride (H<sup>-</sup>) rather than as H<sup>+</sup> would give the metal the oxidation state M<sup>(n+2)+</sup>. It is this very ambiguity, however, that is key to the action of such metals as catalysts, since the MH<sub>2</sub><sup>n+</sup> ion can undergo "reductive" elimination of H<sub>2</sub> to give M<sup>n+</sup> again.

An alternative manner of activating the coordinated CO toward reaction with water would be to protonate the metal center or cluster (eq 14). Given the for-



malisms regarding coordinated hydrogen mentioned above, this also represents oxidation of the metal. However, regardless of the semantics, the increased positive charge at the metal center and corresponding decreased backbonding into the carbonyl should serve to activate the CO toward nucleophilic attack. Of course, H<sub>2</sub> elimination, not CO activation, is rate limiting in the ruthenium cluster catalyzed WGS described above. In this context, we must consider the possibility that a similar process may be the key to catalysis in acidic solution as well. In such a case major shifts in equilibria such as eq 15 might have substantial



effects on the catalytic activity if the anion and neutral show significantly different propensities toward H<sub>2</sub> elimination.

Active solutions of the Eisenberg catalyst<sup>4</sup> (prepared from [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>, glacial acetic acid, concentrated HCl, and NaI in water) contain only monomeric rhodium species, RhI<sub>2</sub>(CO)<sub>2</sub><sup>-</sup>, RhI<sub>5</sub>(CO)<sub>2</sub><sup>2-</sup>, and RhI<sub>4</sub>(CO)<sub>2</sub><sup>-</sup> being the principal components. Both the relative concentrations of these species and the activities of the system are complicated functions of the reaction variables (temperature, P<sub>CO</sub>, [H<sup>+</sup>], [I<sup>-</sup>], etc.). Nonetheless, the two key processes are CO reduction of Rh(III) to Rh(I) and H<sub>2</sub>O oxidation of Rh(I) back to Rh(III) (eq 16 and 17).



Attempts in this laboratory to exploit an acidic medium for WGS catalysis with simple carbonyls have met with mixed success. For example, catalyst solutions prepared from Ir<sub>4</sub>(CO)<sub>12</sub> or Fe(CO)<sub>5</sub> in a H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/ethoxyethanol solution proved inactive at temperatures where the same carbonyls showed significant activity in alkaline solution.<sup>10,25</sup> However, analogous solutions prepared from Ru<sub>3</sub>(CO)<sub>12</sub> did prove active although unstable owing to the sublimation of Ru<sub>3</sub>(CO)<sub>12</sub> out of the reaction solution. Nearly identical be-

havior was noted when the tetrahydride H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> was used as the starting complex. In this context several other solvents were explored, and diglyme was found to be effective in forming an active, moderately stable, ruthenium carbonyl based catalyst in acidic solution.<sup>10</sup> For example, a solution prepared from Ru<sub>3</sub>(CO)<sub>12</sub> (0.0064 M), H<sub>2</sub>SO<sub>4</sub> (0.5 N), and H<sub>2</sub>O (8 M) in 100 °C diglyme under 1.0 atm of CO gave a consistent activity of about 60 mol of H<sub>2</sub> per mol of Ru<sub>3</sub>(CO)<sub>12</sub> per day.

The nature of the ruthenium carbonyl based catalyst in acidic diglyme has been and is the subject of lengthy study in this laboratory. A key observation is that solutions of Ru<sub>3</sub>(CO)<sub>12</sub> in acidic aqueous diglyme show virtually no catalytic activity initially when heated at 100 °C under a CO atmosphere. Some CO<sub>2</sub> production is noted even in the early stage, but significant H<sub>2</sub> production does not begin for a minimum of several hours after the start of a run. Over the same time frame, the Ru<sub>3</sub>(CO)<sub>12</sub> undergoes complete conversion to other species, as reflected by the decrease in the characteristic absorption band of this cluster at 394 nm. Although there was increased absorbance in the UV region at wavelengths below 300 nm, no new absorption maxima could be discerned. Similar spectral changes are seen when Ru<sub>3</sub>(CO)<sub>12</sub> dissolved in octane or concentrated H<sub>2</sub>SO<sub>4</sub> (which is principally the protonated species HRu<sub>3</sub>(CO)<sub>12</sub><sup>+</sup> under the latter conditions) is irradiated with visible light.<sup>26</sup> In the former case, the photochemical product is known to be Ru(CO)<sub>5</sub>.<sup>27</sup> Similarly, given the assignment of the 394 nm band of Ru<sub>3</sub>(CO)<sub>12</sub> as a σ → σ\* transition<sup>28</sup> and the observation that other ruthenium clusters of nuclearity three or greater show similar near-UV or visible absorption bands, the photoproduct in H<sub>2</sub>SO<sub>4</sub> is also believed to be mononuclear or, at largest, dinuclear. An analogous argument would seem appropriate for the nature of the ruthenium carbonyl species in the acidic catalyst solutions.

Extensive kinetics studies have been carried out on the acidic ruthenium carbonyl system in aqueous diglyme using batch reactor techniques and are now in progress using continuous flow reactors.<sup>29</sup> From the results of the batch reactor runs, the following qualitative observations can be made: At low CO pressures (less than ~1 atm) the catalysis is first order in ruthenium concentration over the range 0.018–0.072 M and in P<sub>CO</sub> but only marginally affected by changes in sulfuric acid and water concentrations over the respective ranges 0.25–2.0 M and 4–12 M. However a dramatic turnaround in activity occurs at CO pressures much larger than 1 atm, with the production of H<sub>2</sub> and CO<sub>2</sub> being inhibited by increasing P<sub>CO</sub> under these conditions. The system is temperature sensitive with an activation energy of about 15 kcal found in the low P<sub>CO</sub> region.

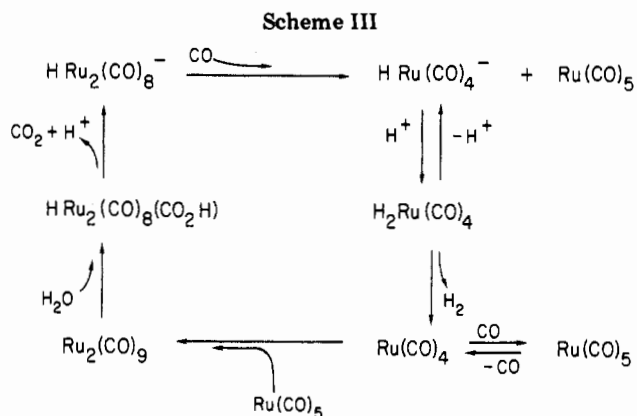
In situ spectroscopic studies on the ruthenium catalyst in acidic aqueous diglyme are currently in progress in our laboratory. A key set of observations derive from

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(27) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, 67, C75 (1974).

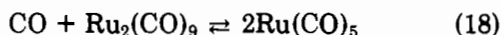
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(29) P. Yarrow, H. Cohen, and P. Ford, manuscript to be published in the A.C.S. Symposium Series Volume "Catalytic Activation of Carbon Monoxide".



the NMR data spectra,  $^1\text{H}$  and  $^{13}\text{C}$ , of an operating catalyst at  $90^\circ\text{C}$  and  $P_{\text{CO}} = 1$  atm which indicate the presence of only one major ruthenium species. The proton spectrum shows a sharp singlet at  $\tau$  24.0 which remains such when the solution is cooled to room temperature, although several other species begin to grow in at these conditions. The  $^2\text{H}$ -decoupled  $^{13}\text{C}$  spectrum also shows a singlet (at 198.2 ppm downfield from  $\text{Me}_4\text{Si}$ ) at both temperatures which becomes a doublet ( $J_{\text{C-H}} = 10$  Hz) when proton coupled. This spectrum is inconsistent with those of  $\text{H}_2\text{Ru}(\text{CO})_4$  or  $\text{HRu}(\text{CO})_5^+$  which would be two key species in a catalysis cycle based on mononuclear species. (The former shows a proton resonance at  $\tau$  17.6, the latter at  $\tau$  17.2, with the  $^{13}\text{C}$  spectrum showing resonances at 180.4 ( $J_{\text{CH}} \leq 4$  Hz) and 178.4 ppm ( $J_{\text{CH}} = 24$  Hz), corresponding to the cis and trans carbonyls, respectively).<sup>30</sup> The catalyst solution  $^{13}\text{C}$  resonance occurs at a position downfield from those found for cationic ruthenium carbonyl hydrides such as  $\text{HRu}(\text{CO})_5^+$  and  $\text{HRu}_3(\text{CO})_{12}^+$  and in a region more consistent with a neutral or anionic species. Attempts to isolate cationic species from the catalyst solution proved unsuccessful; however, the addition of large cations such as  $\text{Ph}_4\text{As}^+$  lead to the precipitation of ruthenium carbonyl anions. Thus we propose the principal component to be the previously unreported dinuclear anion  $\text{HRu}_2(\text{CO})_8^-$  and that a cycle such as Scheme III may be operating in the present case. The iron analogue of this ion has been characterized, and its NMR spectrum also shows but one  $^{13}\text{C}$  resonance even at low temperature ( $-70^\circ\text{C}$ ) owing to the fluxional character of the metal carbonyl bonds.<sup>31</sup>

The key features of the mechanism represented by Scheme III are that at low  $P_{\text{CO}}$  the ruthenium is tied up largely as the  $\text{HRu}_2(\text{CO})_8^-$  ion and the rate-limiting step is the reaction of this ion with CO to break the metal-metal linkage to give  $\text{Ru}(\text{CO})_5$  plus  $\text{HRu}(\text{CO})_4^-$ . Under such conditions the rate should be first order in both  $[\text{Ru}]$  and  $P_{\text{CO}}$ . The  $\text{HRu}(\text{CO})_4^-$  ion would be sufficiently basic to undergo protonation and give the dihydride which loses dihydrogen. Inhibition of catalysis at high  $P_{\text{CO}}$  may reflect conditions where the equilibrium



becomes a dominant factor in the catalysis. Support for this proposition comes from the flow reactor kinetics currently in progress. At very low ruthenium concen-

trations, first-order behavior in  $[\text{Ru}]$  apparently no longer holds and the reaction kinetics indicate orders closer to two than one, thus supporting the possible importance of eq 18 to the overall catalysis rate under these conditions. Further supporting evidence comes from a complication in the flow reactor kinetics. These systems show slow decreases of activity over a period of time owing to the loss of ruthenium from the solution, a problem especially apparent at high  $P_{\text{CO}}$ . Examination of a low-temperature trap downstream from the catalysis vessel showed the presence of a clear solution, mostly diglyme, which when warmed to room temperature turned yellow and slowly precipitated  $\text{Ru}_3(\text{CO})_{12}$ . Thus the gas stream of the flow system served to sweep a volatile ruthenium species out of the reaction solution probably as  $\text{Ru}(\text{CO})_5$  or  $\text{H}_2\text{Ru}(\text{CO})_4$ .

### Retrospection and Prospectus

It is clear from the preceding discussion that a number of chemical systems are active for homogeneous, solution phase catalysis of the water gas shift reaction. In a sense, these have been "discovered" over the past several years; however, there was considerable earlier evidence and speculation that such a process would be viable. There are several themes which do emerge from the current work. Catalysis of the shift reaction appears to be a quite general property of carbonyl complexes in alkaline solutions. The key mechanistic steps for which some kinetics information is available are the activation of coordinated CO by reaction with hydroxide<sup>32</sup> and the reductive elimination of dihydrogen from a resulting metal hydride. Which of these is rate limiting in a cycle such as Scheme I or some variation thereof is a function of the specific metal system and the specific reaction conditions. Notably, a basic solution is not a necessary condition for WGS catalysis. Although WGS catalysis is not as general a phenomenon in acidic media, several such systems have been characterized with activities which compare very favorably to those seen in basic solutions.

While logical mechanisms have been proposed for several of the better characterized catalysts, it is clear that a more complete mechanistic understanding of the key steps in potential cycles is greatly needed. In our laboratory, recognition of such needs has led to fundamental studies into the acid/base natures of metal carbonyl hydride clusters, of CO activation on cluster and mononuclear metal carbonyls by bases, and of dihydrogen elimination from and declusterification and clusterification reactions of metal carbonyl hydrides. While none of these processes is in itself catalytic, the sum of several represents possible cycles. Thus it is hoped that, by dissecting the whole beast into functionally significant parts, the operation of the whole might be better understood.

With regard to the future of homogeneous WGS catalysts, it is obvious that under the conditions which these have been tested, the known systems are not commercially viable. Certainly, for a reaction such as the WGS for which effective heterogeneous catalysts are known, it will take substantial advantages for a new system to be an attractive alternative to established technology. In this context the insensitivity toward

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(31) J. P. Collman, R. G. Fincke, P. L. Matlock, R. Wahren, R. G. Kanote, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978).

(32) In amine solutions, there is not sufficient evidence to differentiate between attack on coordinated CO by equilibrium concentration of  $\text{OH}^-$  or a mechanism involving initial attack by the ammine (see ref 11a).

several homogeneous WGSR catalysts toward sulfide poisoning<sup>11b,33</sup> may represent the appropriate type of advantage. However, even greater benefit may derive from "spin-off" technology, examples being the demonstrations of the activity of WGSR catalysts for other homogeneous catalysis applications such as the hydroformylation<sup>5,6j</sup> and hydrogenation<sup>34</sup> of olefins, as well

(33) A. D. King, R. B. King, and D. B. Yang, *J. Chem. Soc., Chem. Commun.*, 529 (1980).

(34) C. H. Cheng, L. Kwirtzkes, and R. Eisenberg, *J. Organomet. Chem.*, 190, C21 (1980).

as providing models for improved understanding and design of heterogeneous catalysts themselves.

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## Reactive Scattering of Ground-State Oxygen Atoms

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The reactions of oxygen atoms in their ground electronic state, O(<sup>3</sup>P), are of great importance in combustion<sup>1</sup> and upper atmosphere<sup>2</sup> chemistry. The kinetics of O atom reactions have been widely studied,<sup>3</sup> especially by the discharge of flow method. However, if we are to understand the interactions which govern these reactions we must seek more detailed information than is available from conventional measurements where the initial properties of product molecules are obscured by subsequent collisions.

Molecular beam reactive scattering experiments offer a powerful method of measuring the properties of product molecules resulting from single reactive collisions. Beams of molecules are formed in an evacuated scattering chamber at pressures which are so low that the mean free path between collisions becomes much greater than the dimensions of the chamber. Two molecular beams intersect in the scattering chamber, and collisions occur only in the intersection zone. The volume of the scattering zone and the densities of molecules in the beams are limited so as to ensure that only single collisions occur. Some of these collisions, usually a very small proportion  $\leq 10^{-4}$ , give rise to reaction. The flux of product molecules recoiling from reactive collisions is measured by a mass spectrometer detector which may be rotated about the scattering center. Hence reactive scattering may be measured as a function of scattering angle. If the scattering is interrupted by a suitable chopper placed in front of the detector, the flight time of product molecules from the chopper to the detector may be determined and from this the molecular recoil velocity may be calculated. Suitable detectors may be devised to identify also the vibrational and rotational states of product molecules.

Roger Grice was born in Ormskirk, Lancs, England. He obtained a B.A. degree from Cambridge University in 1963 and a Ph.D. degree, as a Frank Knox Memorial Fellow supervised by D. R. Herschbach, from Harvard University in 1967. Following postdoctoral work at Bonn University with J. P. Toennies, he served on the faculty at Bristol University and then at Cambridge University before being appointed to the Chair of Physical Chemistry at Manchester in 1976. He was awarded the Marlow Medal and Prize for 1974 and the Corday Morgan Medal and Prize for 1976 by the Chemical Society.

Indeed, any property of the scattered molecules may in principle be determined by the molecular beam method, though practical experiments are usually limited to the simultaneous measurement of two or perhaps three variables.

The earliest molecular beam studies of O atom reactive scattering used a low-pressure discharge source of O atoms to study the reactions of halogen molecules<sup>4</sup> and also thermal dissociation of O<sub>2</sub> in a high-temperature iridium oven was used to study the reactions of CS<sub>2</sub> and I<sub>2</sub> molecules.<sup>5</sup> However, these early experiments using effusive O atom beam sources did not always permit a full resolution of the differential reaction cross sections at a specific initial translational energy. This was due to the Maxwell-Boltzmann velocity distribution of the O atom beams and the lack of a ready means of varying the initial translational energy of the reactive collisions. Velocity distributions of product scattering were measured for the reactions of O atoms with halogen molecules,<sup>4</sup> but the conventional single-slot time-of-flight method employed was inefficient and was not applicable to reactions with less intense reactive scattering. Thus these pioneering experiments, while demonstrating many fascinating features of O atom reaction dynamics, underlined the need for improved experimental techniques which would allow more detailed investigation of a wider range of reactions.

The dynamics of O(<sup>3</sup>P) atom reactions are of particular interest since the reactants approach on a triplet potential-energy surface which correlates with reaction products but which is above a singlet potential-energy surface as illustrated in Figure 1. The singlet poten-

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