Communications to the Editor

Homogeneous Catalysis of the Water Gas Shift Reaction Using Rhodium Carbonyl Iodide

Sir:

The water gas shift reaction, eq 1,

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \tag{1}$$

has been of great industrial importance for over 40 years.[1] The reaction finds application in the large scale production of hydrogen for ammonia synthesis,[2] in increasing the H_2:CO ratio for methanation and Fischer-Tropsch synthesis,[1] and in the treatment of combustion exhaust gases through CO removal and H_2 generation for reducing nitrogen and sulfur oxides.[3] Heterogeneous catalysts for eq 1 fall into two distinct categories, based either on Fe_3O_4 and related oxides at temperatures exceeding 350 °C, or on copper metal in the range 200-250 °C.[2] Under ambient conditions, the reaction is slightly favored thermodynamically ($\Delta H°_{298} = +0.68$ kcal/mol; $\Delta G°_{298} = -4.76$ kcal/mol), but at higher temperatures the equilibrium becomes significantly less favorable for product formation (K equals 1.45×10^3 and 26.9 at 127 and 327 °C, respectively[4]). The mechanism of the heterogeneously catalyzed reaction has been much studied.[2,5] To date, few reports have appeared on the homogeneous catalysis of eq 1,[6-8] the most recent one being by Ford and co-workers using $Ru_3(CO)_{12}$.[8] We herein wish to report a more active homogeneous catalyst system for the water gas shift reaction which functions at low temperatures (<95 °C), and which, based on known rhodium complex chemistry,[9-13] allows a reasonable proposal for the mechanism of the observed catalysis.

The catalyst system is prepared under N_2 from $[Rh(CO)_2Cl]_2$[14] (97 mg, 0.5 mmol of Rh), glacial acetic acid (26 mL), concentrated HCl (12 mL), NaI (16.8 g), and H_2O (12 mL); the solution is filtered to remove precipitated NaCl and any undissolved NaI. Catalysis of eq 1 was established in the following way. The catalyst solution was placed in a 1-L flask which was evacuated, flushed once with CO, and then charged at room temperature to an initial CO pressure of 250-400 Torr. Approximately 50 Torr of N_2 was then added as an internal calibrant for GC analysis. The solution was heated with stirring to 90 (±2) °C for run I, and 80 (±2) °C for run II. The gases above the intensely brown solution were sampled periodically using a Pressure-Lok syringe, and analyzed by gas chromatography.[15,16] At the end of each run, the solution was cooled to room temperature, and a final gas sample was withdrawn and analyzed. The solution used for run I was recharged with CO, and the results of run III produced. The nature of the products was verified mass spectrometrically, while the quantitative data were obtained from GC analysis.[16] Table I presents the amounts of H_2 and CO_2 produced together with CO consumed for each of the runs, while Figure 1 shows the change in gas composition as a function of time for an additional run. The results clearly establish the stoichiometry as that of the water gas shift reaction, and the product totals correspond to ca. nine turnovers per day for run I with no loss of activity upon recharging.

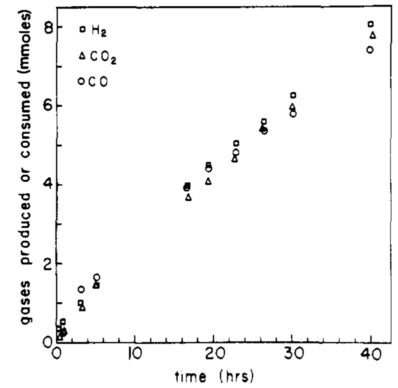


Figure 1. Production of H_2 and CO_2 and consumption of CO for a single run at 90 °C. All CO data take into account the CO initially liberated by the Rh(I) carbonyl iodide anion in eq 2. *Initial* CO in this run was 267 Torr or 16.1 mmol and the amount of Rh catalyst was 0.5 mmol.

In order to probe the essential features and requirements of the catalyst system, a number of controls and related experiments were performed leading to the following observations: (i) in the absence of I^-, the solution remained yellow and no products were observed; (ii) substitution of HBF_4 for HCl yielded a dark brown, catalytically active solution, while omission of a strong acid produced only a trace of CO_2 and a yellow solution; (iii) reaction solutions with acetic acid present were three-five times more reactive than in its absence; (iv) the use of ^{13}CO yielded CO_2 product having the same abundance (4.15%) of ^{13}C label as the reactant CO (3.92%); and (v) in the absence of CO gas, the catalyst solution under N_2 yielded stoichiometric amounts of H_2 and CO in a 1:1 ratio, followed by slow conversion of the liberated CO to CO_2. Observations (i) and (ii) indicate that both H_3O^+ and I^- are necessary for the observed catalysis. However, the direct use of commercial aqueous HI in the preparation of the catalyst system was avoided because the H_3PO_2 preservative it contains leads to spurious results.

The established chemistry of rhodium complexes makes possible a detailed proposal for the mechanism of the observed catalysis. Product formation occurs in distinct steps, with the catalytically active species alternating between the Rh(I) and Rh(III) oxidation states. In the presence of excess I^-, the Rh(I) complex in solution is undoubtedly $[RhI_2(CO)_2]^-$. This species is the only rhodium(I) carbonyl halide that reacts with its respective hydrohalogenic acid, yielding a dark brown Rh(III)

Table I. Results of Catalytic Runs of the Water Gas Shift Reaction

Run	Time, h	Temp, (±2 °C)	CO[a] (consumed)	H_2[a]	CO_2[a]	Cycles/day[b]
I	43	90	6.4	7.8	7.7	8.6
II	78	80	8.7	8.2	7.9	5.0
III[c]	45	90	7.6	8.4	8.6	9.0

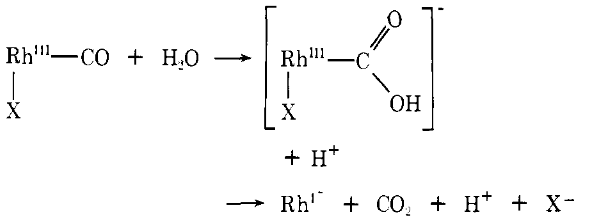
[a] In millimoles. [b] Per millimole of rhodium. [c] Recharge of run I.

carbonyl iodide and H_2 according to eq 2.[12] This reaction, which was first reported by Vallarino[10] and later by Forster,[12] is verified by observation (v). The initial step of eq 2 unquestionably involves protonation by a strong acid. The formation of H_2 may then follow via a hydride/iodide interchange with hydride transfer from Rh(III) to H^+. Dihydrogen is thus produced by the reduction of protons with concomitant oxidation of Rh(I) to Rh(III). Iodide coordination is necessary for this process.

$$[RhI_2(CO)_2]^- + 2HI + aI^- \rightarrow [RhI_b(CO)]^{c-} + H_2 + CO \quad (2)$$

$$(a = 0, 1; b = 4, 5; c = 1, 2)$$

The production of CO_2 takes place by nucleophilic attack of water on a Rh(III)-coordinated carbonyl, eq 3. Activation of the CO ligand to nucleophilic attack is achieved through its coordination to a metal ion in a higher oxidation state which reduces back-donation and increases the residual positive charge on the carbonyl carbon donor atom. This notion receives strong support from numerous sources including (a) the known CO reduction of hydrated $RhCl_3$,[9] (b) an ^{18}O labeling study[17] of the $[RhCl_2(CO)_2]^-$ catalyzed reduction of NO by CO which shows the product CO_2 to contain a labeled oxygen from cocatalyst water, and (c) the ferricyanide oxidation of CO to CO_2 catalyzed by a cobalt carbonyl cyanide species.[18] The Rh(I) anion produced in eq 3 is then able to coordinate a CO ligand, completing the catalytic cycle.


(3)

Alternative schemes can be proposed. For example, if X in eq 3 is a hydride and CO_2 production proceeds via a β-elimination from a heteroatom, a Rh(III) dihydride is produced which can reductively eliminate H_2 and regenerate a Rh(I) species. In this scheme, the formation of the Rh(III) carbonyl hydride also involves protonation, and the production of H_2 remains intimately tied to the reactivity of the Rh(I) center. In yet another scheme the catalytic cycle stays entirely in the Rh(III) regime with CO_2 production proceeding via heteroatom β-elimination to produce a Rh(III) hydride, and H_2 production occurring by hydride transfer from Rh(III) to H^+. Addition of CO to give a Rh(III) carbonyl then completes the cycle.

Observation (iv) unequivocally establishes that CO is the source of the product CO_2, thus ruling out any possible involvement of acetic acid in this regard. That acetic acid enhances the activity of the catalyst system is shown by observation (iii). The role of acetic acid is as yet undefined, but it may relate to the influence of the ancillary ligands on the reactivity of the rhodium center in each of its oxidation states. While I^- activates the Rh(I) center to protonation, it deactivates the Rh(III)-CO moiety to nucleophilic attack by water, thus permitting the isolation of Rh(III) carbonyl iodides, such as $[RhI_5(CO)]^{2-}$.[12] Substitution of acetic acid for iodide, however, may facilitate aqueous attack on the coordinated carbonyl and lead to CO_2 formation by eq 3.

It seems certain that optimization of the observed catalysis will be closely related to understanding how the ancillary ligands influence the reactivity of the catalytically active center in its different oxidation states.

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Retention of Stereochemistry in the Extrusion of Sulfur Monoxide from Thiirane Oxides. Synthesis and Thermal Decomposition of *cis*- and *trans*-Dideuteriothiirane Oxide

Sir:

The mechanism of the thermal decomposition of thiirane oxides, potentially valuable sources of sulfur monoxide in solution, has been a matter of considerable controversy. Unimolecular decomposition of the parent thiirane oxide[1] ($E_a \approx 35$ kcal/mol) is expected to result in the "spin-allowed" formation of both singlet ethylene and sulfur monoxide, the latter being an excited state species quite possibly accessible thermodynamically.[2-4] However, attempts to detect singlet sulfur monoxide by physical (microwave, EPR)[5] or chemical means (trapping with dienes[4,6] or trienes,[7] respectively) have provided evidence best accommodated by the assumption of the intermediacy of the corresponding ground state triplet species. Similarly, decomposition of stereochemically labeled thiirane oxides (*cis*- and *trans*-diphenyl-,[8] or dimethylthiirane oxide[9]) resulting in ethylene products in which stereochemical integrity has been lost has been interpreted as a process in which sequential carbon-sulfur bond breaking proceeds via a diradical intermediate.