Volume 20
Number 3
March 1981

Inorganic Chemistry

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Ionic Attachment as a Feasible Approach to Heterogenizing Anionic Solution Catalysts. Carbonylation of Methanol

RUSSELL S. DRAGO,* ERIC D. NYBERG, ANTON EL A'MMA, and ALAN ZOMBECK

Received April 2, 1980

Few definitive examples of ionically supported anionic transition-metal complexes for use in catalysis have been reported, even though there are several advantages to be gained from such systems. To demonstrate the feasibility and usefulness of such materials in catalysis, we investigated the $[Rh(CO)_2I_2]^-$ catalyzed carbonylation of methanol to acetic acid. The ionically supported $[Rh(CO)_2I_2]^-$ species was found to be equal in catalytic activity to the homogeneous complex, and leaching of the catalyst could be minimized by suitable choice of solvent and resin:rhodium ratios. Additionally, we investigated the usefulness of a solid-phase acid in catalyzing the formation of CH_3I from NaI (NaI by itself is inactive). We found this acid catalyst was active in this regard and that the acidity was retained within the solid phase. These experiments suggest a general application of anion-exchange resins as a mechanistic tool for detecting catalysis by anionic species in homogeneous processes.

Introduction

The advantages of heterogenizing homogeneous catalysts are well documented,[1] and numerous examples of the successful application of this concept to many different catalytic systems have been reported.[2] Covalent attachment of the catalyst to the polymer support is generally utilized, and examples of ionically bound polymer supported catalysts are seldom found. To date anion-exchange resins have been used to support mononuclear transition-metal ions such as $PtCl_4^{2-}$, $PdCl_4^{2-}$, and $RhCl_6^{3-}$[2e] for use as hydrogenation catalysts. A cation-exchange resin has been used to support Rh_2^{4+}.[3] More recently rhodium clusters have been supported on an Amberlyst A-21 resin[4] (a polystyrene resin functionalized with *N,N*-dimethylbenzylamine groups). Neutral clusters were employed which underwent reaction upon attachment. It was proposed that ionic species formed in the reactions were converted to neutral rhodium–nitrogen adducts to account for the retention of the metal. The authors stated that they were uncertain about the identity of the active catalytic (hydrogenation) species. Presumably the lack of ionic systems is due to doubts about the lability of the ionic bonds in solution as well as concern about possible rate-inhibiting effects resulting from increased charge delocalization on oxidatively adding a substrate to the catalyst. The small number of ionically supported systems reported encouraged us to attempt the preparation of such catalysts and to investigate the leaching characteristics of the materials.

There are several advantages in demonstrating the stability of ionically bound catalysts. Many transition-metal catalyst systems involve ionic complexes that react with neutral, nonpolar, substrates leading to problems with their mutual solubility in one solvent. Ionic attachment of the catalyst to a support has the advantage of dispersing the metal anions so that most of the catalyst in the swollen polymer is accessible to neutral, nonpolar substrates. Additionally, ionic polymer supports may be of value in trapping ionic catalysts and inhibiting second-order decomposition reactions. Capturing ionic solution catalysts and transferring their activity to a solid can provide an important tool for characterizing the charge of the catalyst in the solution reaction.

To demonstrate the feasibility and practicality of ionically binding catalysts, we chose the $[Rh(CO)_2I_2]^-$ catalyzed carbonylation of methanol to acetic acid. There were several reasons for choosing this particular system. First, the homogeneous reaction has been thoroughly studied,[5] enabling us to start on a firm mechanistic ground. Second, the solvent system for this reaction is very polar and contains several potential counterions which could conceivably substitute for the $[Rh(CO)_2I_2]^-$ species, resulting in its leaching into solution. This feature allowed us to determine the practicality of ionically supporting a catalyst under the least favorable conditions. Third, the rate-determining step of this reaction involves an increase in the coordination number of the catalyst,[6] offering an opportunity to detect negative rate effects resulting from an increased ionic size. Fourth, several attempts have already been made to heterogenize active rhodium species, and all have met with only limited success. The first example[7] involved the use of rhodium nitrate and $[Rh(CO)_2I_2]^-$ impregnated on activated charcoal. The latter was found to exhibit identical

---

(1) (a) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1978**, 15, 73. (b) Grubbs, R. H. *CHEMTECH* **1977**, 512.

(2) See, for example: (a) Bailar, John C., Jr. *Catal. Rev.—Sci. Eng.* **1974**, *10*, 17. (b) Leznoff, C. C. *Chem. Soc. Rev.* **1974**, *3*, 65. (c) Pittman, C. U., Jr.; Evans, G. V. *CHEMTECH* **1973**, 560. (d) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135. (e) *Prog. Polym. Sci.* **1977**, *5*, 95–226. (f) Card, R. S.; Neckers, D. C. *J. Am. Chem. Soc.* **1977**, *99*, 7734.

(3) Tegzdins, P.; Mitchell, R. W.; Rempel, G. L.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 3322.

(4) (a) Kitamura, T.; et al. *Chem. Lett.* **1975**, 203. (b) Pittman, C. U.; et al. *J. Mol. Catal.* **1979**, *5*, 319.

(5) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 225.

(6) Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846.

(7) Schultz, R. G.; Montgomery, P. D. *J. Catal.* **1969**, *13*, 105.

0020-1669/81/1320-0641$01.00/0 © 1981 American Chemical Society

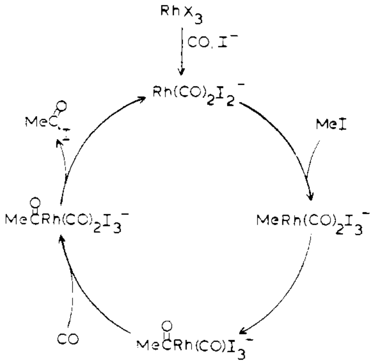

Figure 1. Mechanism of the carbonylation of methanol by $[Rh(CO)_2I_2]^-$.

reaction order dependencies.[8] Gates et al. found extensive leaching of a covalently bound rhodium species.[9] Catalysts showing activity for the carbonylation of methanol have been produced by incorporating rhodium into various zeolites.[10-12] The most recent example has been reported by Scurnell and Howe. Finally, the choice of this system gave us an opportunity to simultaneously investigate the effectiveness of a solid-phase acid catalyst on the formation of the promoter, CH_3I, from sodium iodide (vide infra). Thus we feel the $[Rh(CO)_2I_2]^-$ catalyzed carbonylation of methanol to acetic acid reaction is well suited for a demonstration of the feasibility and value of ionically binding a catalyst to a polymer support.

The mechanism of the homogeneous reaction is well understood (see Figure 1). A wide variety of rhodium catalyst precursors may be used, all of which form the active catalyst $[Rh(CO)_2I_2]^-$ in the presence of CO and I^-.[13] This anionic species oxidatively adds CH_3I (promoter) as evidenced by infrared and product isolation.[6] Kinetic studies indicate the oxidative addition of CH_3I to the $[Rh(CO)_2I_2]^-$ species is the rate-determining step; the carbonylation reaction follows the rate expression[13] (eq 1). Further kinetic studies[14] by

$$\text{rate} = k[[Rh(CO)_2I_2]^-][CH_3I] \qquad (1)$$

Hjortkjaen and Jensen found $k = k_0 \exp(-E/RT)$ where $k_0 = 3.5 \times 10^6$ L/(mol s) and $E = 14.7$ kcal/mol. In the presence of excess CO, the $[Rh(CO)_2(I)_3(CH_3)]^-$ complex inserts CO into the Rh–CH_3 bond, adds CO, and reductively eliminates acetyl iodide. The free acetyl iodide undergoes a substitution reaction with methanol or water, forming methyl acetate or acetic acid and regenerating free HI.[6]

Methyl iodide can be formed from methanol with a variety of substances[13] (HI, $CaI_2 \cdot 2H_2O$, I_2) (eq 2). The reaction

$$CH_3OH + I^- \rightleftharpoons CH_3I + OH^- \qquad (2)$$

requires Lewis or Bronsted acid catalysis. The equilibrium lies far to the right[5] and is attained rapidly at the temperature of the carbonylation process (120 °C). Sodium iodide, in the absence of acid, is not an effective promoter for CH_3I formation.[5] Interest in a solid-phase acid catalyst for the formation of CH_3I from NaI is due to the highly corrosive nature of the acidic homogeneous solution.[15] The solid-phase acid should retain its acidity within the solid phase, thus reducing the corrosive nature of the solution.

Results and Discussion

Preparation and Characterization of the Catalyst. The rhodium catalyst was heterogenized by reacting ion-exchange resins (Bio Rex 9, Dowex 1-X8, or a copolymer of styrene and 4-vinylpyridine alkylated with methyl iodide, forming a methylpyridinium functionalized polymer) with $[Rh(CO)_2Cl]_2$ in the absence of CO and iodide or $RhCl_3 \cdot 3H_2O$ in the presence of excesses of these reagents. This in situ catalyst generation was preferred over preliminary supported catalyst synthesis and isolation because of the greater control of the rhodium concentration for each catalytic run. Resins with the yellow color characteristic of the $[Rh(CO)_2X_2]^-$ ($X = Cl^-, I^-$) species[16] were obtained from both rhodium precursors. Isolation of th yellow resin was straightforward for the catalyst derived from the rhodium dimer, and its infrared spectrum exhibited CO stretching bands at 1981 and 2065 cm^{-1} which are in good agreement with those reported for the tetraphenylarsonium salt of $[Rh(CO)_2I_2]^-$ (at 1988 and 2060 cm^{-1} in CH_3COOH).[16] However, isolation of the yellow catalyst derived from $RhCl_3 \cdot 3H_3O$ in excess CO and iodide resulted in an immediate decomposition of the catalyst to a red species with a CO band observed at 2040 cm^{-1}. This reversible decomposition has been previously reported[16] (reaction 3) and

$$2[Rh(CO)_2I_2]^- + 6I^- + 4H^+ + O_2 \rightleftharpoons 2[Rh(CO)I_5]^{2-} + 2CO + 2H_2O \qquad (3)$$

the red product characterized as $[Rh(CO)I_5]^{2-}$ (infrared band at ~2040 cm^{-1}). The yellow species could be isolated after the polymer-supported red complex was reimmersed in methanol under CO at room temperature and again after the yellow beads were filtered in the absence of excess iodide. Carbonyl bands were observed at 1980 and 2050 cm^{-1} in the infrared spectrum of this supported catalyst, again supporting the identification of the supported yellow complex as $[Rh(CO)_2I_2]^-$.

The rhodium complex is concluded to be ionically bound, and not simply trapped, because in the preparation of the catalyst nearly all of the rhodium is extracted from the solution onto the beads as evidenced by lack of catalytic activity in the filtrate (vide infra).

Catalytic Runs. Catalysts were compared by monitoring the CO pressure drop after NMR, IR, and GLC methods demonstrated that acetic acid and methyl acetate were the sole products of the catalytic reaction. Data which permit a comparison of the homogeneous and supported systems are contained in Table I. The rates of carbonylation of methanol for the supported systems are equal, within experimental error, to those for the homogeneous systems as seen by comparison of run 1 with runs 2 and 3, as well as run 10 with run 11. This similarity in rates is an unusual finding for supported catalysts because either the structure of the catalytic species is modified upon heterogenizing or diffusion of the reactants through the polymer to the catalyst becomes rate controlling. Grubbs et al. found inhibition of catalytic reaction rates occurred because of diffusion problems with hydrocarbons containing six or more carbon atoms.[17] The smaller molecules involved in our system (CO, CH_3I), even with a much higher gel resin crosslinking (8%) and a poorer swelling solvent, do not seem to exhibit diffusion-controlled reaction rates, as judged from the similarity in the reaction rates for both the homogeneous and supported systems. At least two examples of supported cationic

---

(8) Roth, J. F.; et. al. *J. Catal.* **1972**, *27*, 389.

(9) Webber, K. M.; Gates, B. C.; Drenth, W. *J. Mol. Catal.* **1977/78**, *3*, 1.

(10) Yashima, Y.; Orikasa, Y.; Takahashi, N.; Hara, N. *J. Catal.* **1979**, *59*, 53.

(11) Christensen, B.; Scurrel, M. S. *J. Chem. Soc., Faraday Trans. 1* **1978**, 75, 2313.

(12) Scurrell, M. S.; Howe, R. F. *J. Mol. Catal.* **1980**, *7*, 535.

(13) Roth, J. F.; Craddock, J. H.; Hershman, A.; Paulik, F. E. *Chem. Technol.* **1971**, 600.

(14) Hjortkjack, J.; Jensen, V. W. *Ind. Eng. Chem. Prod. Res. Dev.* **1976**, *15*, 46.

(15) See, for example: Matsuhira, N.; Ono, U. *Chem. Abstr.* **1979**, *90*, 121-23b.

(16) Forster, D. *Inorg. Chem.* **1969**, *8*, 2556.

(17) Grubbs, R. H.; Kroll, L. C.; Sweet, E. H. *J. Macromol. Sci., Chem.* **1973**, *A7*(5), 1047.

Table I. Polymer Bound and Solution Catalysts for the Carbonylation of Methanol

run	mmol of $RhCl_3 \cdot 3H_2O$	mol of I (source)	time of run, min	ΔP_{CO}, psi	additional reagents
1 (H)[a]	0.190	0.20 (HI), 0.03 (CH_3I)	68	9	solvent A[c]
2 (P)[b]	0.190	0.20 (HI), 0.03 (CH_3I)	68	11	solvent A, 0.50 g of Dowex 1-X8 (iodo form)
3 (P)	0.190	0.20 (HI), 0.03 (CH_3I)	68	10	solvent A, 2.00 g of Dowex 1-X8 (iodo form)
4 (P)	0.190	0.20 (HI), 0.03 (CH_3I)	136	20	solvent A, 2.00 g of Dowex 1-X8 (iodo form) (same soln as in run 3)
5 (H)	filtrate from run 4	0.20 (HI), 0.03 (CH_3I)	136	5	solvent A (no Dowex)
6 (P)	0.190	0.20 (HI), 0.03 (CH_3I)	120	15	145 mL of 60:40 benzene/CH_3OH, 2.00 g of Dowex 1-X8 (iodo form)
7 (H)	filtrate from run 6	0.20 (HI), 0.03 (CH_3I)	120	1	145 mL of 60:40 benzene/CH_3OH (no Dowex)
8 (P)	0.390	0.31 (HI)	90	15	30 mL of CH_3COOH, 20 mL of CH_3OH, 5.00 g of BioRex 9 (Cl form)
9 (H)	filtrate from run 8	0.31 (HI)	180	0	30 mL of CH_3COOH, 20 mL of CH_3OH (no BioRex 9)
10 (H)	0.380	0.20 (HI), 0.03 (CH_3I)	68	23	solvent A
11 (P)	0.380	0.20 (HI), 0.03 (CH_3I)	68	22	solvent A, 4.00 g of Dowex (same soln as in run 10)

[a] (H) indicates a homogeneous reaction. [b] (P) indicates a polymer-supported reaction. [c] 60 mL of CH_3COOH, 60 mL of CH_3OH, and 25 mL of H_2O.

Table II. Methanol Carbonylation with Supported Promoters and Iodide Sources

run	mmol of $RhCl_3 \cdot 3H_2O$	mol of I (source)	time of run, h	ΔP_{CO}, psi	additional reagents
12	0.190	0.040 (NaI)	10	0	100 mL of CH_3OH
13	0.190	0.040 (NaI)	12	1	100 mL of CH_3OH, 2.0 g of sieves
14	0.190	0.040 (NaI)	21	7	100 mL of CH_3OH, 7.0 g of sieves (21 mmol of H^+)
15	0.28	0.011 (on Dowex beads)	24	0	60 mL of CH_3COOH, 60 mL of CH_3OH, 42 mL of H_2O, 4.00 g of Dowex (iodo form)
16	0.190	0.013 (on Dowex beads)	25	5	100 mL of CH_3OH, 5.00 g of Dowex (iodo form), 10.0 g of sieves
17	0.190	0.040 (NaI)	21	12	100 mL of CH_3OH, 21 mmol of HNO_3
18	0.190	0.040 (I_2)	10	12	100 mL of CH_3OH
19	0.190	0.160 (CH_3I)	3	28	50 mL of CH_3OH, 2.00 g of Dowex (iodo form)

complex systems in which the catalytic activity is different than their homogeneous counterparts have been reported. Wilkinson et al. exchanged a Rh_2^{4+} cation on a Dowex resin and found that in the presence of $(C_6H_5)_3P$ this resin was 1/40th as active as the homogeneous counterpart in the hydrogenation of 1-hexene.[3] Intercalated cationic rhodium species have been reported that are twice as effective as the homogeneous catalyst.[18]

The equivalence of both the homogeneous and supported catalytic rates supports our earlier conclusion that the same catalytic species is present in both systems. These data also indicate there is no significant decrease in rate from an ion-pairing energy change due to increased ionic size from the oxidative addition of CH_3I to the rhodium anion. The delocalization of the $[Rh(CO)_2I_2]^-$ complex's negative charge on oxidative addition may be expected to result in a decreased electrostatic interaction with the polymer support's cationic function and thus in an energy destabilization in the rate-determining step of this reaction.

The rate law for the supported system appears to be first order in $[Rh(CO)_2I_2]^-$ in runs 3 and 11 where doubling the amount of the supported catalyst (by doubling the $RhCl_3$ and Dowex bead concentrations) resulted in an approximate doubling of the reaction rate. This result suggests that a liquid-flow system design in which there is a large catalyst to methanol ratio could prove to be a very effective method for carrying out the reaction. Such ratios are limited in the homogeneous system by catalyst solubility. This apparent similarity of reaction order in rhodium, as well as the equivalence of the homogeneous and supported catalysts' rates, supports our characterization of the ionically bound species as $[Rh(CO)_2I_2]^-$.

As evidenced by run 5, leaching of the catalyst did occur with the conditions employed in run 4. For determination of the effectiveness of lowering the solvent dielectric on the extent of leaching, runs 6 and 7 were conducted. These indicate that substituting a benzene/methanol solvent (in a 60:40 volume ratio) for the acetic acid/methanol/water solvent, with otherwise identical conditions, results in a drop in leaching from 25% to 7% with little attendant rate reduction. It is important to note runs 8 and 9 demonstrate leaching may be minimized. Here the polymer weight to solution volume ratio was increased and the dielectric of the solvent decreased (in relation to runs 4 and 5). A catalytic run with the filtrate from run 8 (run 9) resulted in no CO pressure drop, even though twice as much time was allowed for the reaction. This result clearly indicates that leaching in ionically supported catalyst systems may be controlled by adding more polymer support, decreasing solution volume, or changing solvent polarity.

Table II contains the results of a series of experiments in which investigations were carried out on the effects of heterogenizing the acid and iodide source. As reported,[5] NaI cannot be used in place of HI, CH_3I, or I_2 (run 12) as a promoter for methyl iodide formation from methanol. The catalytic effect of adding activated molecular sieves (solid-phase acid) to the solution of run 13 is demonstrated in run

---

(18) Quayle, W. H.; Pinnavaia, T. J. *Inorg. Chem.* **1979**, 18 2840.

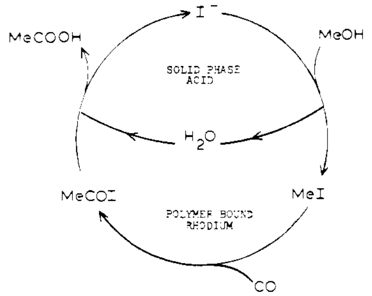

Figure 2. Catalytic cycles: top, solid-phase acid catalyzes the formation of CH_3I; bottom, polymer-bound $[Rh(CO)_2I_2]^-$ catalyzes the carbonylation.

14. Thus catalysis of reaction 2 can be carried out by a heterogeneous phase that contains an acid (see Figure 2). A titration of the sieves before and after catalysis establishes that the acidity remains in the heterogeneous phase, thus avoiding the problems associated with high solution acidity. Even with 7.0 g of sieves, the rate of CO uptake is much slower than when I_2 or CH_3I was used (runs 18 and 19). This is due to a low concentration of protons from the 7 g of sieves. At low $[H^+]$ the rate of carbonylation of methanol is limited by the rate of formation of methyl iodide from sodium iodide. The formation of methyl iodide was verified with both GLC and NMR methods. An equivalent number of protons from HNO_3 were more efficient at CH_3I formation than the molecular sieve source (run 17 compared to run 14).

When Dowex 1-X8 supported I^- and $[Rh(CO)_2I_2]^-$ was used without a Lewis acid (run 15), no pressure drop was observed, and analysis of the solution showed no CH_3I. However, when 10.0 g of sieves were added to a solution of Dowex-supported I^- and $[Rh(CO)_2I_2]^-$ (run 16) catalysis did occur, and the GLC indicated a small amount of CH_3I present in solution. The CH_3I formed must have resulted from diffusion of I^- into the sieves and illustrates the dynamic nature of Dowex-bound I^-.

We have demonstrated the ionic attachment of a rhodium catalyst to a polymer exhibits catalytic rates comparable to the solution analogue and that leaching can be minimized under suitable conditions. We have also shown that solid-phase acids are effective in converting sodium iodide to methyl iodide. More importantly, this study serves to further demonstrate the potential value of ionically supported catalysts in general and will hopefully spur more work in this neglected area.

Experimental Section

Materials. Methyl iodide (Eastman Kodak), rhodium chloride trihydrate (Alfa Products), hydriodic acid, sodium iodide (Mallinckrodt), and all solvents were of reagent grade and used without further purification.

The iodide form of the Dowex 1-X8 anionic exchange resin (200–400 mesh) was prepared by stirring Soxhlet-extracted (4:1 dioxane/H_2O) chloride-form beads with a 10-fold excess of NaI in an acetone/H_2O solvent for 2 days, further Soxhlet extracting, and oven-drying at 70 °C. (Anal. Found: I, 34.6; Cl, 0.3.) Polystyrene-bound methylpyridinium iodide was prepared by the addition of polystyrene-bound pyridine (1.0 g) to a stirred solution of benzene (20 mL) and methyl iodide (5.0 mL). This was refluxed for 23 h, collected by suction, and air-dried. Bio-Rex 9 was used as the chloride form after Soxhlet extracting for 2 days.

The catalyst, $[Rh(CO)_2I_2]^-$, was prepared in situ before each run from $RhCl_3 \cdot 3H_2O$, I^-, and CO in the presence of all other solvents and reagents used in a particular run, at a temperature of either 25 or 120 °C depending on the speed of its formation. For example when HI was used, catalyst formation occurred in 30 min at 25 °C, while with NaI it required ≈5 h at 120 °C. Catalyst formation was indicated by its characteristic yellow color.

The solid-phase acid was generated from Linde Molecular Sieve Catalyst Base LZ-Y62 powder on heating at 400 °C for 3 days, resulting in the loss of ammonia from the ammonium counterion function of the sieves and leaving behind caged protons. The time of heating controls the acidity of the sieves, and we were able to drive off nearly stoichiometric quantities of ammonia, generating a solid phase with approximately 2–3 mmol of H^+/g of sieves as determined by titration with a sodium hydroxide solution.

Apparatus. All catalytic runs were carried out in a 500-mL Parr pressure bottle equipped with a 200-psi Marsh pressure gauge and gas inlet–outlet tube for filling and purging. The bottle–copper tubing interface was sealed by a tightly clamped silicone rubber stopper. No pressure drop occurred from the sealed system in 24 h on pressurization to 120 psi at either RT or 120 °C. The apparatus was checked for leaks every five or six runs to insure there were no spurious pressure drops.

Contributions to ΔP_{CO} from both CO concentration and solution vapor pressure changes during the reaction were considered and found to be negligible for all pressure drops. At the temperature employed for the runs (120 °C) the steady-state concentration of CH_3I was achieved in a negligible amount of time (except when NaI was used), as determined from identical pressure drops for consecutive runs of the same solution.

Catalytic Runs. A typical catalytic run was carried out as follows. To a 500-mL Parr pressure bottle were added 0.100 g of $RhCl_3 \cdot 3H_2O$, 4.00 g of Dowex 1-X8 (iodide form), 60 mL of CH_3COOH, 60 mL of CH_3OH, 25.0 g of HI, 2.0 mL of CH_3I, and a magnetic stirring bar. The bottle was connected to the pressure apparatus previously described and purged 6 times with 100 psi of CO at room temperature over a period of 30 min. The solution was then stirred until it turned orange or light yellow (30 min to 3 h depending on amount of Dowex resin present), the pressure was lowered to precisely 80 psi of CO, the system was equilibrated, the apparatus was placed in a preheated oil bath at 120 °C, and the solution was vigorously stirred. After 68 min in the 120 °C bath the apparatus was removed and immediately place in an ice-water bath for 15 min with continued stirring for fast reaction termination. The final pressure was read 1 h later at room temperature.

The GLC spectra were recorded on a Varian Model 940 FID instrument at 55 or 80 °C using a 1 m, $^1/_{16}$ in. id copper column packed with Chromasorb P supported diethylene glycol adipate. All infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 599B, and the NMR spectra were recorded on a Varian 390. The production of acetic acid and methyl acetate was confirmed by NMR, GLC, and IR methods, as well as from their characteristic odors and the CO pressure drops. Methyl iodide formation was confirmed by both GLC and NMR methods.

Acknowledgment. The authors acknowledge the financial support of this research by the Office of Naval Research.

Registry No. CH_3OH, 67-56-1; CO, 630-08-0; $[Rh(CO)_2I_2]^-$, 38255-39-9; CH_3I, 74-88-4; NaI, 7681-82-5.