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Catalytic Hydrogenation of Carbon Monoxide with $Ir_4(CO)_{12}$ and $AlCl_3$

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The catalytic hydrogenation of carbon monoxide in a NaCl–$AlCl_3$ melt using $Ir_4(CO)_{12}$ as the primary catalyst precursor is described. Under flow conditions at 1 atm pressure, the optimum reaction temperature was 170–180 °C; turnover rates were $\sim$0.2 min^{-1} on the basis of $Ir_4(CO)_{12}$. Products were methane, ethane, propane, butane, isobutane, isopentane, neopentane, methylcyclopentane, trimethylbutane, methylcyclohexane, and dimethylcyclohexanes. The major products were isobutane and propane. Spectroscopic studies showed that $Ir_4(CO)_{12}$ was converted to new iridium carbonyl complexes under reaction conditions. In the absence of a CO–H_2 atmosphere, these iridium carbonyl complexes decomposed irreversibly at reaction temperatures; the resultant system was then inactive for carbon monoxide hydrogenation. Product distribution was primarily affected by variations in contact times: long contact times favored ethane formation. The catalytic system also converted hydrogen and methyl derivatives like trimethylaluminum and trimethoxyaluminum to similar hydrocarbon mixtures.

Introduction

A hydrocarbon solution of $Ir_4(CO)_{12}$ converted a CO–H_2 gas mixture to methane and ethane at 160–180 °C and 1–2 atm, but the rate was exceedingly low.[1,2] The reaction was too slow under these conditions to be amenable to mechanistic studies. Later we[3] found that the $Ir_4(CO)_{12}$ catalyst precursor was exceptionally active when the solvent was the eutectic NaCl–$AlCl_3$ mixture. We describe here a detailed analysis of this catalytic system. A formally analogous system based on $Os_3(CO)_{12}$ and a boron trihalide reaction medium will be reported elsewhere.[4]

Experimental Section

Materials. $Ir_4(CO)_{12}$ was purchased from Pressure Chemical Co. and was used without further purification. Analytical reagent grade $AlCl_3$ (Mallinckrodt Chemical Co.) and $AlBr_3$ (Alfa) were sublimed twice at $\sim$150 °C (10^{-3} torr) prior to use. Analytical reagent grade NaCl and NaBr (Mallinckrodt Chemical Co.) were dried at 100 °C for 4 h. The CO–H_2 gas mixture used in these studies was purchased from Matheson Gas Products; the composition was approximately 25% CO and 75% H_2. Methanol (reagent grade), methyl chloride (Matheson Gas Products), trimethylaluminum (Ethyl Corp.), and trimethoxyaluminum (ICN Pharmaceuticals inc.) were used without further purification.

Apparatus and General Procedure. A schematic representation of the catalytic flow-reaction apparatus is illustrated in Figure 1. In a nitrogen-filled glovebag 40 mg of $Ir_4(CO)_{12}$ and 4 g of a finely ground eutectic mixture of 67% $AlCl_3$ and 33% NaCl (mole percent) were placed in the reactor above frit C. After a thorough flush of the entire apparatus (ca. 30 min.) with a CO–H_2 gas mixture, the reactor portion was immersed into an oil bath which was preheated to a desired reaction temperature. Sampling of the gas phase beyond the reactor was achieved through the serum cap of sampling port E by using a 0.5-mL gas-tight syringe.

Analytical Procedure. Gaseous products were analyzed on a Perkin-Elmer Sigma 3 (flame ionization detector) gas chromatograph by using a 6 × $^1/_8$ in. Porapak Q column at 100 °C. A Finnigan GC mass spectrometer was used for final verification of the products. Residues from the catalytic reactions were examined for metal carbonyl absorptions on a Perkin-Elmer 283 infrared spectrophotometer.

Results and Discussion

Table I. Hydrocarbon Products[a]

compd	% yield	compd	% yield
methane	1.5	neo- and isopentane	17
ethane	1.5	methylcyclopentane	6
propane	17	methylcyclohexane and trimethylbutane	<1
butane	2		
isobutane	54	dimethylcyclohexane (2 isomers)	<1

[a] No alkyl halides or alcohols were detected. Percentages may be converted into turnovers by multiplying by the overall turnover rate.

Catalytic hydrogenation of carbon monoxide by $Ir_4(CO)_{12}$ dissolved in the NaCl–$AlCl_3$ melt proceeded under flow conditions with relatively high rates at quite mild reaction conditions of 125–210 °C and 1 atm pressure. The product was a complex mixture of saturated hydrocarbons that ranged from C_1, methane, to C_8, dimethylcyclohexane. Hydrogen chloride was a coproduct, but its formation was not quantitatively monitored because adventitious moisture was an additional source of HCl and because HCl is very soluble in the reaction medium.

The catalytic reaction initially was very fast, but after 1 h the hydrocarbon production rate dropped substantially and then continued at a sustained level for many days as illustrated in Figure 2. The sharp decrease in initial rate coincided with the conversion of $Ir_4(CO)_{12}$ to new iridium carbonyl complexes which were not as effective as catalyst precursors (see later discussion of spectroscopic studies). At the sustained level of catalytic hydrogenation, the turnover rate at 170 °C was 0.2/min/mol of $Ir_4(CO)_{12}$ initially charged (on the basis of mol of CO converted to saturated hydrocarbons). This turnover rate dropped by 1 to several orders of magnitude at 125 °C and also decreased with temperature increase above 170 °C. At $\sim$210 °C, the partial pressure of CO of 0.25 atm was insufficient to prevent iridium carbonyl decomposition (see spectroscopic discussion below), and the catalytic reaction greatly slowed at these temperatures with the formation of iridium metal. Substitution of finely divided iridium metal for $Ir_4(CO)_{12}$ gave an essentially inactive system (static reaction system at 170 °C).[3] In the absence of $Ir_4(CO)_{12}$, the otherwise complete reaction system yielded no hydrocarbons. With D_2 instead of H_2 as the reactant in the CO–$Ir_4(CO)_{12}$–$AlCl_3$ reaction system, the products were the corresponding perdeuteriohydrocarbons. With CO enriched in ^{13}C (static reaction system), the hydrocarbon products were enriched in ^{13}C. Carbon monoxide reagent is the sole source of the carbon in the hydrocarbon products. In the reduction of carbon monoxide, the oxygen was converted to an Al–O bond; hence the aluminum trichloride was slowly consumed in the reaction.

The character of the saturated hydrocarbon products was a function of reaction time, temperature, and contact time. As can be seen in Figures 2 and 3, propane was the major product at 135 and 170 °C during the initial fast reaction (first hour of reaction), but later isobutane became the major

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(1) Thomas, M. G.; Beier, B. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976** *98*, 4645.
(2) Schunn, R. A.; Demitras, G. C.; Choi, H. W.; Muetterties, E. L. *Inorg. Chem.*, in press.
(3) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796.
(4) Choi, H. W.; Muetterties, E. L. *Inorg. Chem.*, following paper in this issue.

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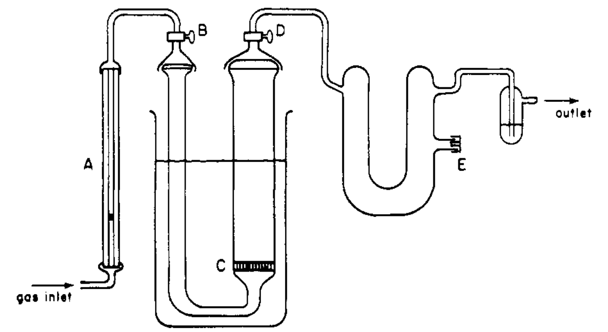

Figure 1. Presented is a sketch of the flow reactor system for the catalytic hydrogenation system.

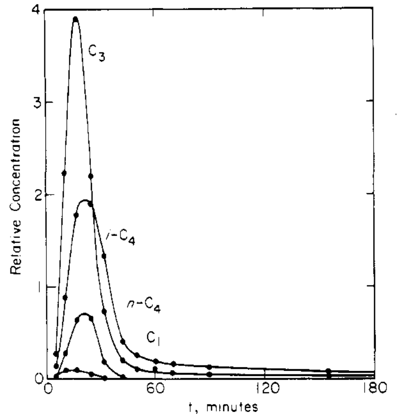

Figure 2. Graph showing the variation in conversion of CO and H_2 to hydrocarbons and the variation in hydrocarbon composition with time at a reaction temperature of 175 °C. The ordinate is in relative molar units, and the abscissa represents the time at which the gaseous product was sampled for analysis.

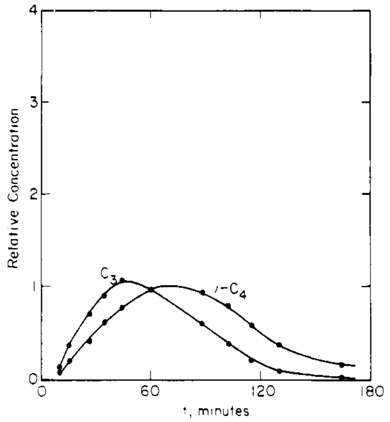

Figure 3. Graph showing the variation in conversion of CO and H_2 to hydrocarbons and the variation in hydrocarbon composition with time at a reaction temperature of 135 °C. The ordinate is in relative molar units, and the abscissa represents the time at which the gaseous product was sampled for analysis.

Table II. Effect of Reaction Temperature on Product Distribution in Catalytic Hydrogenation

	product compn, mol %[a]		
hydrocarbon	160 °C	185 °C	200 °C
CH_4	10	14	25
C_2H_6	5	4	6
C_3H_8	25	36	32
i-C_4H_{10}	45	36	36
n-C_4H_{10}	2	4	2
C_5	7	7	0
C_6	6	0	0

[a] Percentages may be converted into turnovers by multiplying by the overall turnover rate.

Table III. Effect of Flow Rate on Product Distribution[a] in Catalytic Hydrogenation

	product compn, mol %[b]			
hydrocarbon	1 mL/min	6.7 mL/min	12 mL/min	20 mL/min
CH_4	33	18	12	13
C_2H_6	53	8	10	7
C_3H_8	10	24	31	30
i-C_4H_{10}	3	44	46	50
n-C_4H_{10}		0		

[a] Sampled after a flow reaction time of >180 min; reaction temperature was 170 °C. [b] Percentages may be converted into turnovers by multiplying by the overall turnover rate.

Table IV. Reaction of Hydrogen with Hydrocarbon and Hydrocarbon Derivatives in NaCl–$AlCl_3$ at 175 °C

reactant hydrocarbon	hydrocarbon products in mol %[d]			
	CH_3Cl	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
CH_3Cl[a]	100	0	0	0
n-C_4H_{10}[b]	0	11	7	82
i-C_4H_{10}[c]	0	6	92	2

[a] High molecular weight hydrocarbons were produced. [b] Sampled after a flow reaction time of 55 min. [c] Sampled after a flow reaction time of 50 min. [d] Convertible into turnovers by multiplying by the overall turnover rates.

product. Within the stabilized reaction regime, the distribution of hydrocarbon products remained constant. Listed in Table I is the distribution of hydrocarbon products for a reaction temperature of 170 °C; the identified products were methane, ethane, propane, butane, isobutane, isopentane, neopentane, methylcyclopentane, trimethylbutane, methylcyclohexane, and dimethylcyclohexane isomers. Temperature had a minor effect on hydrocarbon product distribution with low temperatures favoring the higher molecular weight hydrocarbons (Table II). Contact time had the most dramatic effect upon product distribution—at least at very long contact times. At long contact times, ethane became the major product (Table III), a feature consistent with our preliminary reports, which were batch, sealed-tube reactions and yielded ethane as the major product. These results were expected since the reaction medium was highly acidic and hydrocarbon cracking reactions should occur. In fact, passage of hydrogen mixtures of either butane or isobutane through the NaCl–$AlCl_3$ solution, in the absence of $Ir_4(CO)_{12}$, gave a low rate of hydrocarbon rearrangement and cracking and explicably butane was more reactive than isobutane (Table IV).

The hydrocarbon product distribution from this catalytic system was unusal with isobutane, the major product, and with the presence of cycloalkanes; similar products were obtained with an $AlBr_3$–NaBr melt reaction system although the relative amounts of methane and ethane were much higher. This feature of the system is attributed to Friedel–Crafts type reactions promoted by the aluminum halide. No hydrocarbon products other than saturated hydrocarbons were produced. A special search was made for CH_3Cl and for methanol (or a methanol precursor such as Al–O–CH_3 species), but neither was detected in the products.

Reaction of methyl derivatives like trimethylaluminum[5] and trimethoxyaluminum[6] with the melt solution of the iridium carbonyl at 175 °C with a nitrogen gas flow led to the production of a saturated hydrocarbon mixture similar in com-

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(5) The flow reactant gas mixture was $(CH_3)_3Al$:H_2:N_2 in a 0.5:15:100 ratio.

(6) $(CH_3O)_3Al$ was added as a solid in a flow of nitrogen.

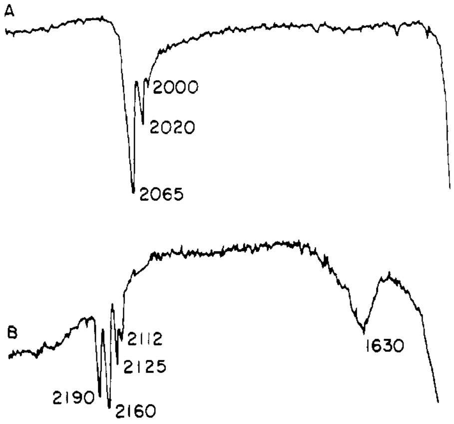

Figure 4. Nujol infrared spectra for $Ir_4(CO)_{12}$ and for a catalyst–melt sample obtained by quenching the reactor at flow reaction times greater than 1 h. Frequencies are in cm^{-1}.

position to that produced in the catalytic system. These experiments thus do not eliminate as possible intermediates in the catalytic reaction species that have Al–CH_3 or Al–OCH_3 bonds. However, the above experiments did exhibit one divergent feature, namely, a disproportionately large amount of methane formation. In the case of $Al(CH_3)_3$, this was largely due to hydrolysis at the glass walls and to reaction with the hydrogen halide, both of which reactions were very fast. We suspect that simple Al–CH_3 or Al–OCH_3 species either are absent in the reaction system or are present only in very low concentrations and that they are not key intermediates in the catalytic sequence.

Methyl chloride was seriously considered as a possible intermediate in the catalytic sequence to at least some of the hydrocarbon products. Reductive elimination of methyl chloride is observed in the decomposition of methyl derivatives of transition-metal chlorides.[7] Second, methyl halides, as well as higher alkyl halides, were products in the catalytic hydrogenation of carbon monoxide based on $Os_3(CO)_{12}$ as the catalyst precursor and boron tribromide as the solvent (and reactant).[4] We found that methyl chloride did react under flow conditions with the $AlCl_3$–NaCl melt in the absence of $Ir_4(CO)_{12}$, although the reaction rate was quite low at 175 °C and no volatile hydrocarabon products were detected. The product was a yellow or orange hydrocarbon derivative. Hence, we can safely state that methyl chloride, in the hydrogenation reaction, is not a key initial product that then undergoes further reaction with aluminum chloride to yield the observed hydrocarbon products.

None of our data provide specific information about the mechanistic features of the catalytic reaction. For the sustained catalytic reaction, tetrairidium dodecacarbonyl is not the catalyst precursor. Infrared investigations showed that a new iridium carbonyl was produced under the reaction conditions. The infrared studies were not effected under reaction conditions but were directed to the melt reaction system—the melt was quenched, isolated, and examined as a Nujol mull. The spectral differences between the cluster carbonyl and those of the iridium carbonyl in the reaction system are shown in Figure 4. The most important feature in the spectrum of the new iridium carbonyl complex(es) was the absorption at 1630 cm^{-1} which is a region characteristic[8] of a carbonyl stretching vibration for a M_xCO–A bonding situation with A, a Lewis acid. In the absence of a CO–H_2 atmosphere, the iridium carbonyl catalyst precursor rapidly decomposed as evidenced by the loss of any absorbance in the CO stretching frequency region. In the *formally* analogous BBr_3–$Os_3(CO)_{12}$ system, the enduring and isolable catalyst precursor was $Os_2(CO)_6Br_4$. Possibly an iridium carbonyl chloride species is the enduring catalyst precursor in this aluminum trichloride system; a supportive experimental observation was the substantial shift in the terminal Ir–CO frequencies to higher energies (Figure 4) in the enduring catalyst precursor (oxidation of the metal center invariably produces such shifts in the CO stretching frequency). The critical role(s) of $AlCl_3$ is not defined by our studies, but we still presume that Ir–C–O–Al interactions are important in the activation of the C–O bond to hydrogenation. Reaction solutions were visibly clear at 125–170 °C, but the absence of light scattering neither precludes the possible presence of very small solid or metallic particles nor the possibility that the catalytic reaction was heterogeneous.

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Registry No. CO, 630-08-0; H_2, 1333-74-0; $Ir_4(CO)_{12}$, 18827-81-1; NaCl, 7647-14-5; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; NaBr, 7647-15-6; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *i*-C_4H_{10}, 75-28-5; *neo*-C_5H_{12}, 463-82-1; *i*-C_5H_{12}, 78-78-4; methylcyclohexane, 108-87-2; trimethylbutane, 464-06-2; dimethylcyclohexane, 27195-67-1; methylcyclopentane, 96-37-7.

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