

THE $Mn_2(CO)_{10}$ CATALYZED HYDROGENATION AND HYDROFORMYLATION OF OLEFINS

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SUMMARY

$Mn_2(CO)_{10}$ catalyze the homogeneous hydrogenation of 1- and 2-octene. In the presence of carbon monoxide and hydrogen at temperatures up to 235°, it is also a homogeneous hydroformylation catalyst. Cyclohexene yields the expected product, cyclohexylmethanol, at 235°, but at 200° the major product is cyclohexylmethyl formate.

INTRODUCTION

A wide variety of complexes derived from Group VIII metals are known to function as hydrogenation and/or hydroformylation (oxo) catalysts¹⁻⁸. In contrast, very little is known about the catalytic activities of Group VII complexes, such as $Mn_2(CO)_{10}$ and its derivatives. A patent⁹ that claims that various derivatives of manganese carbonyl, including $HMn(CO)_5$ and $CpMn(CO)_5$, are good oxo catalysts and a report¹⁰ that $HMn(CO)_5$ shows only slight activity as an oxo catalyst are the only references to $Mn_2(CO)_{10}$ and its derivatives as oxo catalysts. To our knowledge, nothing has been published on $Mn_2(CO)_{10}$ as a hydrogenation catalyst. In the present paper, we report the results of a study of $Mn_2(CO)_{10}$ as a catalyst for the hydrogenation and hydroformylation of olefins.

RESULTS AND DISCUSSION

Results of the $Mn_2(CO)_{10}$ catalyzed hydrogenation of 1- and 2-octene in some solvents are summarized in Tables 1 and 2. As expected, 1-octene is hydrogenated at a faster rate than 2-octene. The relative rates of hydrogenation for both 1- and 2-octene are faster in dioxane than in benzene or methylcyclohexane, but the effect of solvent on rate is small. The extent of isomerization of unreacted olefin is unusually small. The

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TABLE 1

DISTRIBUTION (%) OF PRODUCTS IN THE CATALYTIC REDUCTION OF 1-OCTENE WITH $Mn_2(CO)_{10}$ ^a

Solvent	Reaction time at 160° (h)	Octane	trans-4-Octene	cis-4-Octene ^b	trans-3-Octene	cis-3-Octene + 1-octene ^c	trans-2-Octene	cis-2-Octene	Relative rate ^d
Methylcyclohexane	1	54.9	0.5	0.1	1.2	35.9	4.6	2.5	
Methylcyclohexane	2	76.7	0.6	0.2	1.0	17.6	2.5	1.4	1.0
Benzene	1.5	80.0	0.6	^b	1.1	13.7	3.0	1.5	1.3
Dioxane	1	90.5	0.6	0.2	1.0	4.9	1.9	0.9	1.7

^a All runs done at 3000 lb/in² H₂ initial pressure. ^b Accurate VPC analysis of cis-4-octene was not possible because of interference from the solvent. ^c More than 95% 1-octene as shown by IR analysis. ^d Relative rate based on uptake of H₂.

TABLE 2

DISTRIBUTION (%) OF PRODUCTS IN THE CATALYTIC REDUCTION OF 2-OCTENE WITH $Mn_2(CO)_{10}$ ^a

Solvent	Reaction time at 160° (h)	Octane	trans-4-Octene	cis-4-Octene	trans-3-Octene	cis-3-Octene + 1-octene ^b	trans-2-Octene	cis-2-Octene	Relative rate ^c
Methylcyclohexane	3	75.2	1.7	0.7	3.2	1.2	8.2	9.8	0.4
Benzene	5	78.2	1.7	^d	3.5	0.6	7.8	7.6	0.3
Dioxane	3	88.8	0.9	0.2	1.0	0.5	3.4	4.5	0.7

^a All runs done at 3000 lb/in² H₂ initial pressure. ^b IR analysis of the product mixture indicated that no terminal olefin was present. ^c Relative rate based on uptake of H₂ and compared with reaction of 1-octene in methylcyclohexane. ^d Accurate VPC analysis of cis-4-octene was not possible because of interference from the solvent.

TABLE 3

EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION (mol %) IN THE HYDROFORMYLATION OF CYCLOHEXENE WITH $Mn_2(CO)_{10}$ ^a

Reaction temp. (°C)	Cyclohexane	Cyclohexene	Cyclohexylcarboxaldehyde	Cyclohexylmethanol	Cyclohexylmethyl formate
162 ^{b,c}		96	4	Trace	Trace
175 ^{c,d}	Trace	90	9	1	Trace
200 ^{b,c}	18	37	4	15	26
200 ^{b,e}	9	82	3	3	3
235 ^{b,c}	47	4	1	40	8

^a All runs done at 3000 lbf/in² 1/1 synthesis gas initial pressure with 32 ml (0.32 mol) cyclohexene. ^b 5.5 h at reaction temperature, heat-up time 1.5 h. ^c 3 g $Mn_2(CO)_{10}$ used. ^d 7.0 h at reaction temperature, heat-up time 1.5 h. ^e 1 g $Mn_2(CO)_{10}$ used.

absence of any oxygenated compounds in the reaction product is noteworthy, in view of the fact that we have found that hydrogenation of olefins in the presence of $Co_2(CO)_8$ and hydrogen produces some oxo products due to the transfer of CO in the catalyst to the olefin.

The 2-octene in each of the runs listed in Table 2 contained 72% *cis*-2-octene and 28% *trans*-2-octene at the start. The composition of the 2-octene after hydrogenation was found to be approximately 46% *trans* and 54% *cis* (Table 2). This probably reflects a preferential hydrogenation of the *cis* isomer and a small amount of *cis* to *trans* isomerization.

Hydroformylation of cyclohexene in hexane with an equimolar mixture of H_2 and CO, and $Mn_2(CO)_{10}$ as catalyst, was carried out at various temperatures. Four products, cyclohexylcarboxaldehyde, cyclohexylmethanol, cyclohexylmethyl formate, and cyclohexane, were identified in the reaction mixture (Table 3) by gas liquid chromatography and mass spectroscopy.

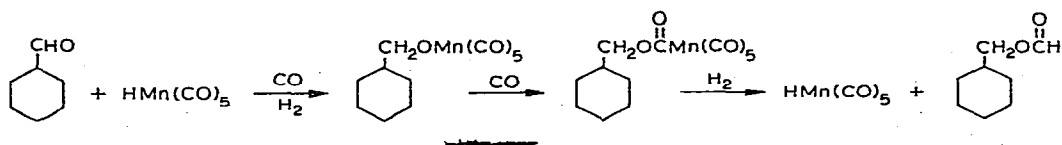
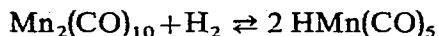
Quantitative recovery of $Mn_2(CO)_{10}$ was not accomplished in any of our reactions and some catalyst appears to have reacted, possibly with the oxygenated oxo products or H_2O . When the hydroformylation was attempted in acetone, extensive decomposition of $Mn_2(CO)_{10}$ occurred, resulting in formation of manganese formate and other insoluble materials thought to be oxides of manganese. Because of the relatively slow rate of reaction (*vide infra*) and its instability, $Mn_2(CO)_{10}$ is not nearly as useful a hydroformylation catalyst as the carbonyls of cobalt and rhodium.

While the cobalt and rhodium carbonyl catalyzed hydroformylation reactions proceed rapidly at 100°^{1,2,11}, the $Mn_2(CO)_{10}$ catalyzed reaction is very slow at temperatures up to 235° and hydrogenation is a competitive reaction. At 200° the major products are cyclohexylmethyl formate and cyclohexane, and at 235° cyclohexylmethanol and cyclohexane. A consequence of the relatively high reaction temperatures is the almost quantitative conversion of the initial oxo product, cyclohexylcarboxaldehyde, to cyclohexylmethanol. In the $Co_2(CO)_8$ catalyzed hydroformylation, aldehydes are reduced to the corresponding alcohols at temperatures as low as 180°¹²⁻¹⁵.

Another characteristic of the $Mn_2(CO)_{10}$ catalyzed hydroformylation of cyclohexene at 200° is the presence of cyclohexylmethyl formate as the major product.

Small amounts of formate ester have been reported in the $\text{Co}_2(\text{CO})_8$ catalyzed reactions of cyclohexene (4–5%), propylene (1.9%), and other olefins^{16,18}; however, to our knowledge it has never been found as the major product of the hydroformylation reaction.

The product distributions obtained at 200° and 235° (Table 3) support the postulation put forth for the case of $\text{Co}_2(\text{CO})_8$, *i.e.*, that cyclohexylcarboxaldehyde is the precursor in formate formation^{17,18}. At 200°, in the case of $\text{Mn}_2(\text{CO})_{10}$ reaction, reduction of aldehyde to the corresponding alcohol is slow and reaction with CO to form the ester can occur. At 235°, the increase in the rate of reduction to alcohol accounts for the decrease in formate formation. A mechanism analogous to that proposed¹⁸ for the cobalt carbonyl catalyzed conversion of aldehyde to formate is applicable to the manganese case.



Further evidence supporting the postulation that cyclohexylcarboxaldehyde is the precursor of cyclohexylmethyl formate was obtained by subjecting cyclohexylcarboxaldehyde and cyclohexylmethanol separately to hydroformylation conditions in the presence of $\text{Mn}_2(\text{CO})_{10}$ at 200°. Seventy-four percent of the aldehyde reacted to give 10% cyclohexylmethyl formate and 64% cyclohexylmethanol. No formate was formed with cyclohexylmethanol as the starting material.

EXPERIMENTAL

Hydrogenation

All hydrogenation reactions were run under the same conditions in a 500 ml Aminco stainless steel rocking autoclave*. To the autoclave were added 150 ml of solvent, 84 g (0.75 mol) of 1- or 2-octene, and 4 g (0.01 mol) of $\text{Mn}_2(\text{CO})_{10}$. Compared to $\text{Co}_2(\text{CO})_8$, $\text{Mn}_2(\text{CO})_{10}$ is stable, if no oxygenated materials are present, in an atmosphere of H_2 under severe reducing conditions. At least 75% of the $\text{Mn}_2(\text{CO})_{10}$ was recovered after each run. The autoclave was flushed several times with H_2 to remove the air, pressured to 3000 lbf/in² H_2 , and heated to 160°. Reaction times and product analyses are listed in Tables 1 and 2. To determine the composition of the unreacted octene mixture, reactions were purposely stopped short of completion. Special care was taken to avoid contamination by other catalysts. The relative rates of hydrogenation were determined by a method previously reported¹¹.

Analysis of the reaction mixtures was done on a Packard Model 7409 gas chromatograph, equipped with a flame ionization detector. The column used was 15 ft by 1/8 in glass, packed with 20% β, β' -oxydipropionitrile and 4.3% silver nitrate on 60–80 mesh Chromosorb P-WA. The various isomers were identified by matching

* Reference to a company or product name is made to facilitate understanding and does not imply endorsement by the U.S. Bureau of Mines.

the retention times of pure octenes with those of the reaction mixture. Mass spectral analysis confirmed the VPC results for the percentage of octane and octenes present in the reaction mixture.

Hydroformylation

To establish whether $Mn_2(CO)_{10}$ can function as a hydroformylation catalyst, it was necessary to exclude rigorously any catalytic effects due to the presence of traces of cobalt. We found that hydroformylation of olefins took place even in the absence of any added catalyst, when the reaction was carried out in autoclaves that had been previously used for hydroformylation in the presence of $Co_2(CO)_8$. Apparently, traces of cobalt retained by the walls of the autoclave were responsible for this catalytic effect. This observation is in agreement with the report by Booth *et al.*¹⁹ on the drastic effect of cobalt on the iron carbonyl catalyzed oxo reaction. Since cleaning the walls of the autoclave did not remove these vestigial effects of cobalt catalysis, we had to run the experiments in a new autoclave. As a further precaution against possible contamination or wall effects, we frequently carried out blank runs using only cyclohexene and hexane.

In a typical experiment, 3 g (0.008 mol) of $Mn_2(CO)_{10}$, 32 ml (0.32 mol) of freshly distilled cyclohexene, and 135 ml of hexane were added to a 500 ml stainless steel rocking autoclave. The autoclave was then flushed several times with 1/1 H_2/CO and pressured to 3000 lbf/in². The various reaction temperatures and times are listed in Table 3.

Product identification was done by comparison of retention times with known samples of the various components and comparison of VPC analysis with infrared and mass spectrometric data.

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