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SUPPORT EFFECTS IN OSMIUM CATALYZED HYDROGENATION AND HYDROGENOLYSIS OF CYCLOPROPANE

Ezekiel O. Odebunmi
Department of Chemistry, University of Ilorin
P.M.B. 1515, Ilorin, Nigeria.

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ABSTRACT. The effect of different metal oxide supports on the rates of reaction between cyclopropane and hydrogen catalyzed by osmium metal was studied in a flow reactor operated at atmospheric pressure, temperature of 40-250°, and reactant gas partial pressure of $0.2 \leq P_{hydrogen} \leq 0.7$ atm and $0.03 < P_{cyclopropane} < 0.11$ atm. The reaction proceeded *via* two different routes: hydrogenation giving propane and hydrogenolysis giving methane and ethane. The products of both reactions were formed from a single surface species. The reaction of cyclopropane with hydrogen to product only methane was not observed on our catalysts. Also the hydrogenolysis of propane and ethane, products of the above reactions, was not significant under reaction conditions. For the two reactions the activity of the catalyst decreased in the order:

$$Os/TiO_2 > Os/SiO_2 > Os/Al_2O_3 > Os/MgO$$

Product selectivity was found to be in favour of hydrogenation and decreased with rise in temperature. The methane-ethane molar ratio was unity and independent of temperature, gas feed composition and flow rate. The observed activity and selectivity patterns are explained in terms of metal support interaction phenomenon.

INTRODUCTION

The reactions of hydrocarbons with hydrogen have often been used as a convenient probe for evaluating catalytic properties of supported metals and clusters because they are structure-sensitive reactions. In addition these reactions are important industrially [1-4]. The reaction of cyclopropane with hydrogen is of interest because it proceeds under fairly mild reaction conditions and gives easily identifiable products. Furthermore it offers an opportunity to investigate both the activity and selectivity of the catalyst.

The products of the reaction of cyclopropane with hydrogen depend on the active metal and support. On platinum, palladium, rhodium and iridium, cyclopropane hydrogenation occurs cleanly to yield propane. However, on nickel, cobalt, ruthenium and osmium, the reaction products include methane and ethane in addition to propane [5-7]. These products are formed from the following reactions:

$$\text{Cyclopropane} + H_2 \dashrightarrow C_3H_8 \quad (1)$$

$$\text{Cyclopropane} + 2H_2 \dashrightarrow CH_4 + C_2H_6 \quad (2)$$

$$\text{Cyclopropane} + 3H_2 \dashrightarrow 3CH_4 \quad (3)$$

Reaction 1 above, leading to the formation of propane, is usually termed hydrogenation while reactions (2) and (3), leading to formation of methane and ethane, are termed hydrogenolysis [15]. On some metals the kinetic analysis is further complicated by the fact that the products of reactions (1) and (2) can react further as follows [3,5]:

$$C_3H_8 + H_2 \longrightarrow CH_4 + C_2H_6 \quad (4)$$
$$C_3H_8 + 2H_2 \longrightarrow 3CH_4 \quad (5)$$
$$C_2H_6 + H_2 \longrightarrow 2CH_4 \quad (6)$$

However the reaction of cyclopropane with hydrogen is faster than either ethane or propane hydrogenolysis [3]. The hydrogenation of cyclopropane to propane on Ni/SiO_2-Al_2O_3 catalyst was reported by Benson and Kwan [8] and the mechanism for the reaction proposed by Bond and Newham [2]. Other investigators have used the hydrogenation and hydrogenolysis of cyclopropane to characterize different catalysts [4,6,9,10]. Extensive reviews are available on hydrogenation and hydrogenolysis reactions [7,11,12].

The influence of the support on the activity of catalysts and their selectivity for specific products is well recognized [13-15]. The support has been implicated as responsible for the variation of activity of supported nickel for ethane hydrogenolysis [15]. The metal-support interaction could be electronic or magnetic and this can modify the catalyst.

The purpose of the present work is to investigate the influence of the support on the activity of osmium catalysts derived from chloroosmic acid ($H_2OsCl_6.6H_2O$) for the hydrogenation and hydrogenolysis of cyclopropane. Towards this end alumina, titania, magnesia and silica were used. The activity of the alumina-supported osmium catalyst derived from osmium pentacarbonyl ($Os(CO)_5$) for the cyclopropane-hydrogen reactions was also investigated.

RESULTS AND DISCUSSION

All the catalysts with the exception of $Os(CO)_5/Al_2O_3$ showed an initially high activity for cyclopropane conversion. This activity decreased with time on stream and levelled off after 1 - 2 hours (Fig. 1). Consequently from plot of activity *vs* time on stream over a two-hour period initial activity levels were determined by extrapolation to zero time. Cyclopropane conversion as a function of the reciprocal space velocity is linear (Fig. 2). This shows that the reactor was operating under essentially differential conversion regime with reaction rates as well as product selectivity being independent of contact time. Reaction rates under these differential conditions were calculated from the equation:

$$\gamma = \frac{FX}{W} \quad (7)$$

where F is moles of feed gas per hr, X is fractional conversion of cyclopropane to propane (hydrogenation) or to methane and ethane (hydrogenolysis), and W is moles of catalyst (osmium metal).

The selectivity to propane, S; was calculated using the equation:

$$S = \frac{rate\ of\ hydrogenation}{total\ rate\ of\ reaction} X\ 100 \quad (8)$$

Where:

total rate of reaction = rate of hydrogenation + rate of hydrogenolysis.

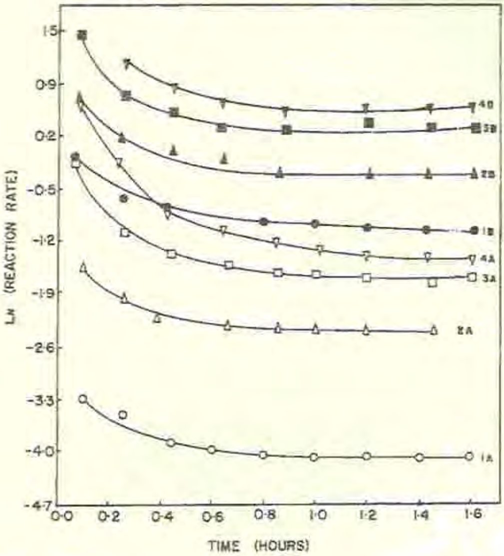

Fig. 1: Os/SiO$_2$ catalyst activity variation with time. 1A, 2A, 3A and 4A represent hydrogenolysis at 40, 50, 60 and 65°, respectively. 1B, 2B, 3B and 4B represent hydrogenation at 40, 50, 60 and 65°, respectively.

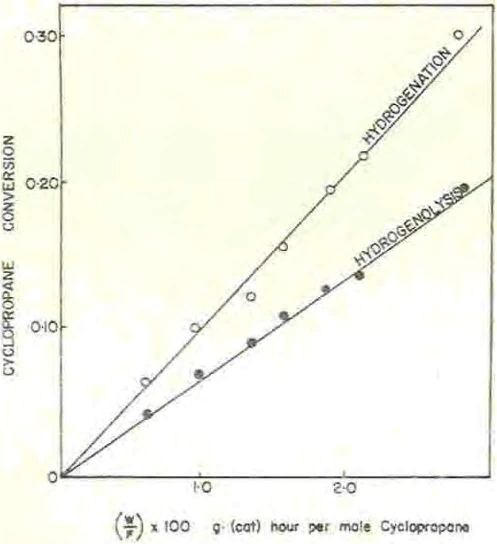

Fig. 2: Cyclopropane conversion *versus* reciprocal space velocity on Os/Al$_2$O$_3$ at 50°.

The rates of the reaction of cyclopropane with hydrogen vary with temperature in the Arrhenius fashion and typical plots are shown in Fig. 3A. Similar typical plots for Os(CO)$_5$/Al$_2$O$_3$ catalyst prior to and after decarbonylation are shown in Fig. 3B. From these plots Arrhenius activation energies and preexponential factors are calculated and summarized in Table 1. In general the apparent activation energy for the hydrogenolysis reaction was higher than that of the hydrogenation, and this explains the observed decrease in selectivity with temperature (Table 2). A plot of ln A, where A is the preexponential factor, against the apparent activation energy E was linear (Fig. 4) clearly demonstrating a compensation effect. Various interpretations have been given to explain the phenomenon of compensation effect as observed in these catalyst system [16-17]. In general a heterogeneous surface is assumed. This surface has a distribution of different active sites with associated activation energy for a particular reaction. The effect of temperature on the distribution of these active sites in the surface presumably results in the compensation effect.

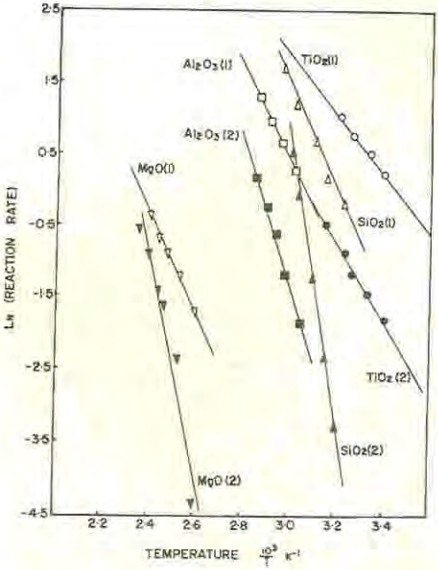

Fig. 3A: Arrhenius plots for Os catalysts derived from H_2OsCl_6 (1) hydrogenation; (2) hydrogenolysis.

Table 1. Arrhenius parameters for osmium catalyzed cyclopropane-hydrogen reactions[a]

Catalyst	Hydrogenation		Hydrogenolysis	
	Activation energy (Kcal/mole)	Preexponential factor (ln A)	Activation energy (Kcal/mole)	Preexponential factor (ln A)
0.66% Os/Al_2O_3	15.5	23.6	23.7	34.0
0.98% Os/SiO_2	16.5	26.5	38.8	54.0
0.98% Os/TiO_2	6.4	11.2	12.8	19.6
0.98% Os/MgO	12.4	14.6	19.5	27.5
0.36%[b] $Os(CO)_5/Al_2O_3$	14.1	14.1	15.0	11.2
0.36%[c] $Os(CO)_5/Al_2O_3$	13.2	21.4	27.0	40.2

[a] Reaction conditions as in Table 4
[b] $Os(CO)_5/Al_2O_3$ prior to decarbonylation
[c] $Os(CO)_5/Al_2O_3$ after decarbonylation

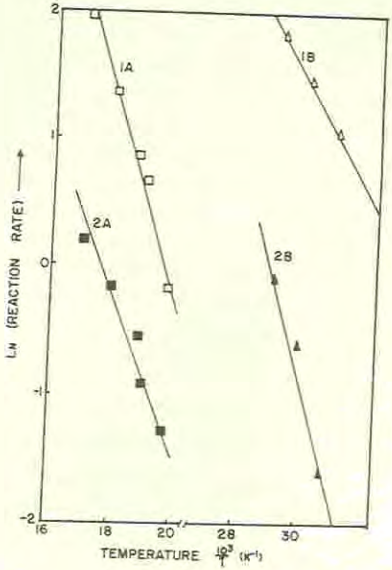

Fig. 3B: Arrhenius plots for Os catalysts derived from $Os(CO)_6$. 1A and 2A: Hydrogenation and hydrogenolysis before decarbonylation of catalyst; 1B and 2B: Hydrogenation and hydrogenolysis after decarbonylation of catalyst.

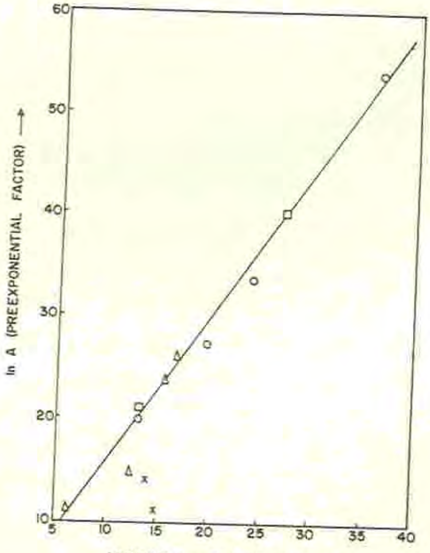

Fig. 4: Compensation effect in hydrogenation and hydrogenolysis of cyclopropane.
Δ Hydrogenation on all catalysts derived from H_2OsCl_6.
○ Hydrogenolysis on all catalysts derived from H_2OsCl_6.
X $Os(CO)_5/Al_2O_3$ before decarbonylation,
☐ $Os(CO)_5/Al_2O_3$ after decarbonylation.

The dependence of the rates of hydrogenation and hydrogenolysis on the hydrogen and cyclopropane partial pressure was examined at 75° in the range $0.3 \leq P_{hydrogen} \leq 0.7$ atm. at cyclopropane partial of 0.03 atm and $0.03 \leq P_{cyclopropane} \leq 0.11$ atm at hydrogen partial pressure of 0.3 atm, with helium gas used as diluent. Kinetic orders with respect to cyclopropane and hydrogen were calculated from the slopes of the plot of the reaction rate *versus* partial pressure of cyclopropane and hydrogen, respectively (Table 3). For all the catalysts the order in cyclopropane was found to be 0.8 to 1.0 for hydrogenation and 0.5 to 0.7 for hydrogenolysis. The order of reaction in hydrogen was less than zero for both hydrogenation and hydrogenolysis. These results agree with literature reports [2,5,6]. For hydrogenolysis of hydrocarbons reaction orders obtained from power law rate equations are known to depend on the composition of the reaction mixture and the conditions [5,6,19]. The data in Table 3 were obtained under hydrogen-rich conditions and the formal reaction order in hydrogen and cyclopropane may be expected to change for cyclopropane-rich reaction mixture.

Table 2. Activity of supported osmium-catalysts for hydrogenation and hydrogenolysis of cyclopropane.

Catalyst	Catalyst activity[b]		Selectivity S^c
	Hydrogenation	Hydrogenolysis	
0.66% Os/Al_2O_3	1.00	1.00	90
0.98% Os/SiO_2	3.2	5.2	88
0.98% Os/TiO_2	4.7	15.2	81
0.98% Os/MgO	0.013	0.0028	55[d]
0.36%[b] $Os(CO)_5/Al_2O_3$			
(i) Before decarbonylation	0.0005	0.0013	74[e]
(ii) After decarbonylation	4.4	3.8	94

[a] Reaction conditions: T = 50°; $P_{(hydrogen)} = 0.7$ atm; $P_{(cyclopropane)} = 0.06$ atm; total pressure = 1 atm.
[b] Activity relative to 0.66% Os/Al_2O_3 with the following rates:
rate of hydrogenation = 0.65 moles propane per mole Os per second rate of hydrogenolysis = 0.05 moles ethane per mole Os per second.
[c] Selectivity, S, as defined in the text (Equation 8).
[d] S determined at 146°.
[e] S determined at 230°.

Table 3. Cyclopropane-hydrogen reactions: Order of reaction in cyclopropane and hydrogen at 75°.

Catalyst	Order of hydrogenation reaction		Order of hydrogenolysis reaction	
	Cyclopropane (m)	Hydrogen (n)	Cyclopropane (m)	Hydrogen (n)
0.66% Os/Al_2O_3	1.0	-0.90	0.70	-1.20
5% Os/Al_2O_3	0.85	-0.67	0.55	-0.90
0.98% Os/SiO_2	0.85	-1.50	0.60	-1.70
0.98% Os/TiO_2	0.90	-1.50	0.70	-1.60
0.98% Os/MgO	0.80	-0.70	0.50	-0.85
0.36%[b] $Os(CO)_5/Al_2O_3$				
(i) Before decarbonylation	0.80	-0.90	0.60	-1.00
(ii) After decarbonylation	1.00	-0.70	0.70	-0.85

[a] Reaction orders m, and n were obtained from the power law rate equation:
Rate = $kP^n_{(hydrogen)}P^m_{(cyclopropane)}$; To determine m, $P_{(hydrogen)} = 0.3$ atm., while $P_{(cyclopropane)} = 0.03 - 0.11$ atm., and to determine n, $P_{(cyclopropane)} = 0.03$ atm. and $P_{(hydrogen)} = 0.3 - 0.7$ atm.
[b] Experiment at 150°.

Methane, ethane and propane were the products obtained during the catalytic conversion of cyclopropane under our experimental conditions. Equimolar amounts of methane and ethane were formed, and the methane to ethane ratio remained unchanged as the temperature, gas feed composition, and flow rates were varied. By contrast the selectivity to propane decreased with increase in temperature. The distribution of products as the temperature, reactant gas partial pressures and flow rates vary indicates that both methane and ethane were formed directly from cyclopropane and that the hydrogenolysis of propane (if it occurred) did not contribute significantly to the methane and ethane formed. The data in Table 2 show clearly that for all the catalysts the selectivity to hydrogenation is higher than to hydrogenolysis. It is well known that the rate of propane hydrogenolysis to methane and ethane is much slower than that of cyclopropane and that on most group VIII metals hydrogenation has higher selectivity than hydrogenolysis [3]. However our present data are not sufficient to carry out a detailed kinetic analysis and hence certain features of the mechanism cannot be addressed.

Table 4. Supported osmium catalysts: Pretreatment and reaction conditions.

Catalyst (precursor/support)	Osmium content	Catalyst pretreatment	Reaction conditions[a]
H_2OsCl_6/Al_2O_3	0.66	1 hr in He at 150° + 10 hrs in H_2 at 400°	50-125°
H_2OsCl_6/Al_2O_3	5.00	1 hr in He at 150° + 10 hrs in H_2 at 400°	50-125°
H_2OsCl_6/SiO_2	0.98	1 hr in He at 150° + 10 hrs in H_2 at 400°	50-125°
H_2OsCl_6/TiO_2	0.98	1 hr in He at 150° + 10 hrs in H_2 at 400°	50-125°
H_2OsCl_6/MgO	0.98	1 hr in He at 150° + 10 hrs in H_2 at 400°	100-160°
$Os(CO)_5/Al_2O_3$	0.36	1 hr in He at 150° + 10 hrs in H_2 at 400°	150-300° before decarbonylation, 40-120° after decarbonylation

[a] Other reaction conditions: hydrogen pressure = 0.2 - 0.7 atm; cyclopropane pressure = 0.03 - 0.11 atm; total pressure = 1 atm; cyclopropane/hydrogen molar ratio = 1 for all experiments.

The activity of all the catalysts for the cyclopropane and hydrogen reactions at 50° and the selectivity to propane are compared in Table 2. The data show that the titania-supported catalyst was the most active and was followed by the catalyst supported on silica, alumina, and finally by magnesia which was the least active. Furthermore hydrogenolysis was more sensitive to the support effect than hydrogenation. All the osmium catalysts derived from chloroosmic acid were more active than $Os(CO)_5/Al_2O_3$ catalyst prior to decarbonylation. After decarbonylation of this catalyst its activity increased becoming similar in magnitude to that of the chloroosmic acid derived catalyst. The decarbonylated catalyst also became as susceptible to deactivation as the supported metals whereas the catalyst prior to decarbonylation was resistant to deactivation. Moreover Fig. 4, illustrating a compensation effect, also shows that the $Os(CO)_5/Al_2O_3$ catalyst could only conform with the other catalysts after it has been decarbonylated. This decarbonylation of alumina-supported osmium carbonyl cluster has been confirmed earlier from Infrared and X-ray photoelectron spectroscopic (XPS) measurements [18,22].

The observed activity of the osmium catalysts could be due to any one or a combination of the following factors:

(i) metal-support interaction phenomenon which could be geometric or electronic and which is known to influence the activity of the supported metals [13-15].

(ii) particle size effect. Both the particle size of the crystallites as well as their dispersion affect the activity and selectivity of catalysts especially for structure-sensitive reactions [3,20].

(iii) the catalyst pretreatment procedure is also well known to influence catalyst activity [13,21]

The presence of residual chlorine in the catalyst could also affect the catalysts activity. Furthermore if the support material reacts with the chlorine during the reduction of the catalyst then the nature and structure of the active sites will change and this could affect the activity of the catalyst.

Our results show clearly the influence of the metal-support interactions on the activity of the supported osmium for the conversion of cyclopropane to propane, methane and ethane. Both XPS and high resolution transmission electron microscopy data indicate ultradispersion of osmium at the low loadings (0.36%, 0.66%, 1%) of the catalyst samples used in these experiments, and that large crystallites are not formed [22]. Thus the catalyst particle size and dispersion could not have played a significant role in the observed activity trend.

All the catalysts used in this study were prepared and pretreated in the same manner with the exception of the osmium pentacarbonyl derived catalyst. After 10 hr reduction in hydrogen at 400° these catalysts are not expected to contain any residual chlorine that could affect the activity of the catalysts. The XPS data confirmed that all the chlorine in the catalyst was virtually removed by the high temperature reduction [18]. Furthermore the lowest activity was observed on the most basic support (magnesia) and this is consistent with the suggestion that the influence of chlorine could not be significant under our conditions. For the hydrogenolysis of ethane and propane on supported ruthenium catalysts it has been reported that catalysts from $RuCl_3.H_2O$ as a precursor showed the same activity pattern as those prepared from osmium pentacarbonyl after complete decarbonylation displayed an activity that was similar to that prepared from chloroosmic acid (Table 2). Therefore we conclude that the strong metal-support interaction was responsible for the activity variation observed during the hydrogenolysis of cyclopropane.

Our results agree with literature reports [3,14,15]. Taylor and co-workers [15] found that for the reaction of cyclopropane with hydrogen on both nickel and cobalt the effectiveness of the various supports decreased in the order:

$$SiO_2 > Al_2O_3 >> SiO_2\text{-}Al_2O_3 > C(\text{carbon})$$

The support also influenced the selectivity of the reaction due to a greater support effect on hydrogenolysis *versus* hydrogenation. They invoked the acidity of the support as the reason of the observed trends. For the hydrogenation of carbon monoxide catalyzed by rhodium metal supported on various metal oxides the support was also found to influence the activity of the catalysts and selectivity to different products, with Rh/TiO_2 being the most active catalyst [14]. For the hydrogenolysis of ethane and propane catalyzed by ruthenium on various metal oxides the activity decreased in the order [3]:

$$SiO_2 > CaO\text{-}MgO > MgO > Al_2O_3 > SiO_2\text{-}Al_2O_3$$

Bossi and coworkers [13] found that the strong interaction between the support and the metal can occur as a function of the nature of the support, the preparation procedure and the activation procedure. We conclude therefore that for our system the nature of the support material has the greater influence on the activity of the osmium catalyst for the hydrogenation and hydrogenolysis of cyclopropane.

EXPERIMENTAL

Materials and catalyst preparation. Chloroosmic acid was obtained from Colonial Metals, Maryland, U.S.A. and used without further purification. The support materials (Magnesia (MgO) MCBX65, 30 m^2/g; Gamma Alumina (Al_2O_3) Ketjen; Titania (TiO_2) Anatase, 53 m^2/g and Silica (SiO_2) Carbosil) were all of commercial grade. Each was treated for several hrs in flowing oxygen at 400° and purged with nitrogen. The catalysts were prepared from chloroosmic acid by aqueous impregnation [20,28]. This involved the complete wetting of the support material with a solution of chloroosmic acid to form a wet paste which was dried at 110° under nitrogen. The dried catalyst was grounded to a fine powder and kept for use. Table 4 summarizes all the catalysts used for this study.

Catalytic reaction rate measurements. The catalytic reaction experiments were carried out in a low pressure differential flow reactor system which was interfaced with an Antek Gas Chromatograph (GC). The reactor, a pipette-shaped 0.4 cm internal diameter pyrex glass tube, was filled with layer of catalyst particles at the centre and held in place by plugs of calcined glass wool at inlet and outlet. Catalyst pretreatment usually involved flushing with helium thoroughly, heating in flowing hydrogen at 400° for over ten hrs, and cooling in hydrogen to the temperature required for the reaction. Catalyst regeneration in between experiments involved heating in hydrogen at 350° for 1 hr. This procedure completely restored catalytic activity and ensured the attainment of reproducible results. The pretreatment of the alumina-supported mononuclear osmium pentacarbonyl catalyst ($Os(CO)_5/Al_2O_3$) also followed the above procedure. However, regeneration of this catalyst was not necessary before decarbonylation. After decarbonylation regeneration was necessary and followed the above procedure.

The experiments were carried out in the temperature range of 40 - 250° while changing the partial pressures of cyclopropane and hydrogen. Helium was used as the diluent. The reactor outlet was injected into an Antek GC equipped with a Flame Ionization Detector via a gas sampling valve. The GC column conditions involved an initial 1 min hold at 40°, temperature programming at 10° per minute to 100°, and then a final 2 min hold at 100°. This ensured the complete separation of the hydrocarbon products on a 1/8" X 6' stainless steel column packed with activated alumina.

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