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SEPARATION OF PIPERYLENE CONCENTRATE
VIA METATHESIS CATALYSIS

BY

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B. S., University of Central Florida, 1978

RESEARCH REPORT

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ABSTRACT

Diolefin metathesis, using a Re_2O_7 catalyst, failed to show a reactivity difference due to conjugation of double bonds. However, the same system allows reaction of pentadiene while not affecting cyclopentene yielding a successful reaction - separation scheme for a piperylene concentrate mixture.

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INTRODUCTION

Piperylene concentrate is the term for a complex mixture of five carbon olefins and diolefins produced as a byproduct during the cracking of naphtha and residual fuel oils. Table 1 shows a typical composition.¹ As the world's supply of natural gas feedstock diminish, liquid feeds must be used to generate ethylene, propylene, and other hydrocarbon gases. A Dow Chemical Company residual fuel oil cracker gives a 24.4% yield of ethylene and a 1.6% yield of piperylene concentrate.²

Ethylene producers are concerned over the large amounts of the piperylene concentrate formed. Because of the similarity of boiling points, Table 1, conventional distillation is inadequate to produce a high purity fraction, and producers must sell the impure byproduct at a lower cost. Currently both major components of the concentrate are used in the pure state to make polymers. Piperylene is used as a

TABLE 1
Composition of Piperylene Concentrate

<u>Compound</u>	<u>Percent by Weight</u>	<u>Boiling Point ($^{\circ}\text{C}$)</u>
<u>trans</u> -1,3-Pentadiene	33.9	42.0
Cyclopentene	27.8	44.3
<u>cis</u> -1,3-Pentadiene	20.4	44.9
2-Methyl-2-butene	10.2	38.6
1,3-Cyclopentadiene	0.8	42.5
2-Methyl-1,3-butadiene	0.5	34.1
Remainder ^a	6.4	

^aRemainder consists of trace amounts of pentane, 2,2-dimethylbutane, cyclopentadiene, and other unidentified hydrocarbons.

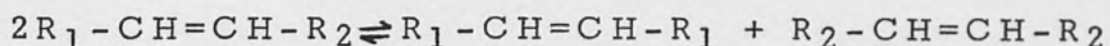
polymeric intermediate and reacted with maleic anhydride to form an epoxy hardener.³ Cyclopentene can be used for a polyolefin rubber, similar to polybutadiene, and also as an epoxy cross-linking agent.³ The current excess piperylene concentrate is simply sold as a fuel, which is not as profitable as using the valuable purified olefins for chemical feedstocks.

Since a simple distillation will not separate the components adequately, a chemical reaction offers the possibility of effecting a separation while maintaining the olefin profitability status of the cracking process. The catalytic metathesis of diolefins was investigated as an attempt to increase the production of ethylene and allow easy distillation separation of the remaining olefin mixture.

Metathesis Reaction

The metathesis is unique in that it maintains the number of double bonds in the reactants. Metathesis is a catalytic reaction where an alkene forms equimolar amounts of two new

alkenes.⁴ The reaction proceeds according to:



Metathesis, disproportionation, and dismutation are all synonyms of the above reaction. Historically, the reaction of a heterogeneous system was termed disproportionation, and that of a homogeneous system was metathesis. However, since disproportionation is not an adequate description of the reaction of two different alkenes, the term metathesis is preferred.⁴ The metathesis reaction was first reported in 1964, when Banks and Baily reported the conversion of propene to ethylene and 2-butene.⁵ Since then the reaction has been used on conjugated dienes,⁶ nonconjugated dienes,⁷ terminal dienes,⁸ cyclic alkenes,⁹ and alkynes.¹⁰ The metathesis reaction has even been used with a Rayonet Photoirradiation reactor.¹¹

Catalysts

Many catalyst systems have been found that will promote the metathesis reaction. The

majority of the heterogeneous catalysts are oxides, carbonyls, or sulfides of the transition metals, deposited on high surface area supports. While molybdenum and tungsten give active catalysts, rhenium stands out as the most active system.⁴ Rhenium oxide (Re_2O_7) on alumina has been found to give yields of 40% and selectivities of 90%, under conditions as mild as 1 atm pressure and 20°C , for a 1-propene feedstream.¹² A patent was granted to British Petroleum for the rhenium oxide catalyst in 1965, and over the next ten years no less than 19 additional patents dealing with improvement to the catalyst system were granted. These improvements included acid pretreatment of the support,¹³ subliming the Re_2O_7 onto the support,¹⁴ and increasing the yield by addition of a small amount of hydrogen to the reaction.¹⁵

Mechanisms

The discovery of a new reaction sparked speculation and indepth mechanistic studies. The initial theories presented a case for

transalkylidation, or reaction across the double bond dealing with pi-bond dissociation. This developed into a mechanism containing a quasi-cyclobutane intermediate.¹⁶ The data suggested that vacant electronic orbitals around the rhenium allow the dissociation of electrons in the olefins to form an unstable cyclobutane intermediate. This then decomposes into new products or the original olefins, Figure 1. Additional studies supported this theory.^{17,18,19}

Currently, the accepted theory deals with the formation of a metal carbene as the intermediate.^{20,21} This theory has also been supported in homogeneous catalytic studies.⁷ The metal forms a carbene with an olefin, effectively splitting the bond. The metal carbene is then allowed to exchange carbene portions with olefins, Figure 2. This implies an initial preparation of catalytic sites.

Thermodynamics

The enthalpy change for a metathesis

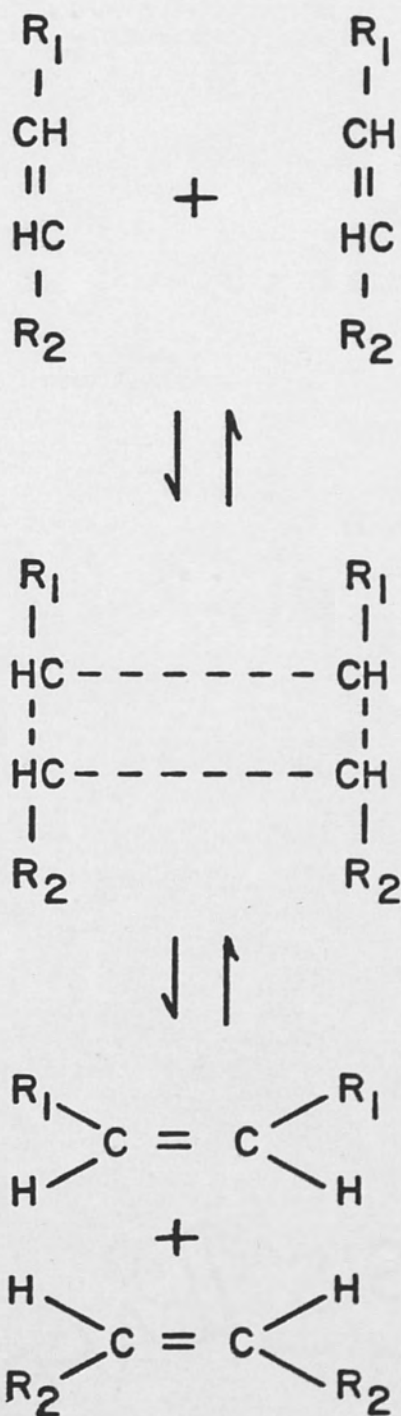
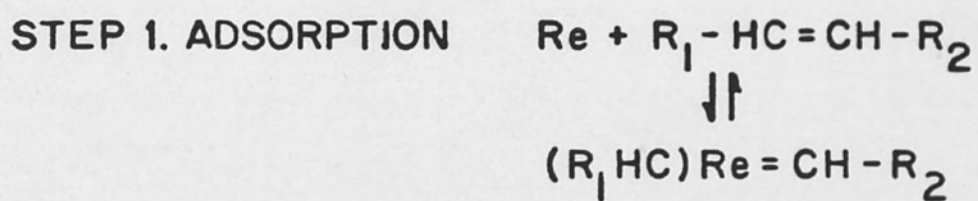


Figure 1. Quasi-Cyclobutane Mechanism



STEP 2. OLEFIN EXCHANGE

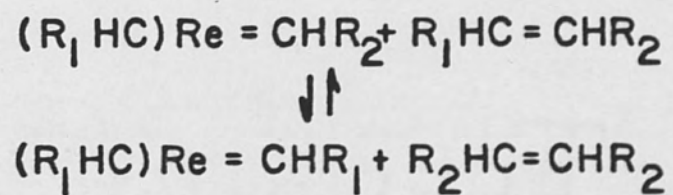


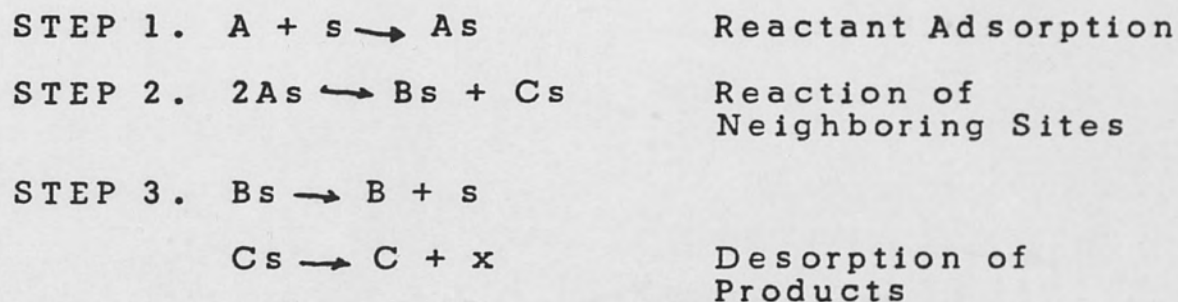
Figure 2. Carbene Mechanism

reaction is nearly zero, due to the total number and types of chemical bonds being equivalent before and after reacting. A basic feature here is that true thermodynamic equilibrium can be obtained rather easily.⁴

Kinetics

The kinetics of heterogeneous metathesis are still questioned. Studies have shown that the surface of metathesis catalysts are truly heterogeneous.²² This implies that kinetic studies have marginal reliability because the actual number of active catalytic sites can increase the temperature.⁴ However, early studies did show that the reaction rate for homogeneous catalyst systems was very high.²⁴

The most accepted kinetic model for heterogeneous catalysis is the Langmuir-Hinshelwood model.⁴ This model, Figure 3, assumes that both reactant molecules must be absorbed onto neighboring active catalyst sites.²³ The reaction then takes place, followed by dissociation of the products from the

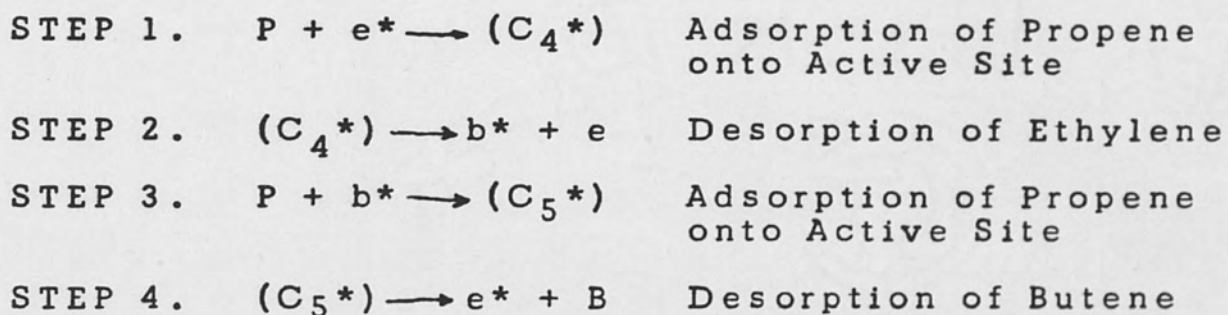


NOTES: 1) s is the catalytic site
2) step 2 is the rate controlling step

Figure 3. Langmuir-Hinshelwood Kinetic Model

catalytic surface. The rate controlling step is thought to be the reaction of neighboring sites.

Recently, the Langmuir-Hinshelwood model was rejected for a rhenium oxide on alumina catalyst system.²⁴ The new Kapteijn model, Figure 4, is based on a non pairwise exchange of alkylidene groups via a carbene species. This model is in agreement with the carbene reaction mechanism and relies on initial preparation of the catalytic sites to form alkylidene carbene surface complexes. For a propene reactant, the active specie is either a methylcarbene or an ethylcarbene. The rate determining steps are considered to be the desorption of each product.



- NOTES:
- 1) e^* is $Re = C$ (methylcarbene).
 - 2) b^* is $Re = CH - CH_3$ (ethylcarbene).
 - 3) The rate determining steps are considered to be steps 2 and 4.

Figure 4. Kapteijn Kinetic Model

EXPERIMENTAL DESCRIPTION

The metathesis reactions were carried out in Pyrex glass tubing. The gases were dried prior to entering the reactor by passing through a gas drier packed with dry calcium sulfate. Connections were accomplished using microware kits. The general schematic of the experimental set up is shown in Figure 5.

Catalyst preparation was based on Turner's patent.⁹ The catalyst was prepared by dissolving ammonium perrheniate, NH_4ReO_4 (Aldrich) in hot deionized water, followed by evaporation onto a chromatographic grade, 80 to 200 mesh, activated alumina (MCB). Initially the amount of hot water able to be absorbed by the alumina was measured. The NH_4ReO_4 was then dissolved in a proportional amount of water and applied to fresh alumina, taking care not to flood the alumina. The absorbed catalyst was then dried in a drying oven at 160°C for at least 24 hours. Turner gave a value of 23.5 gms of Re_2O_7 per

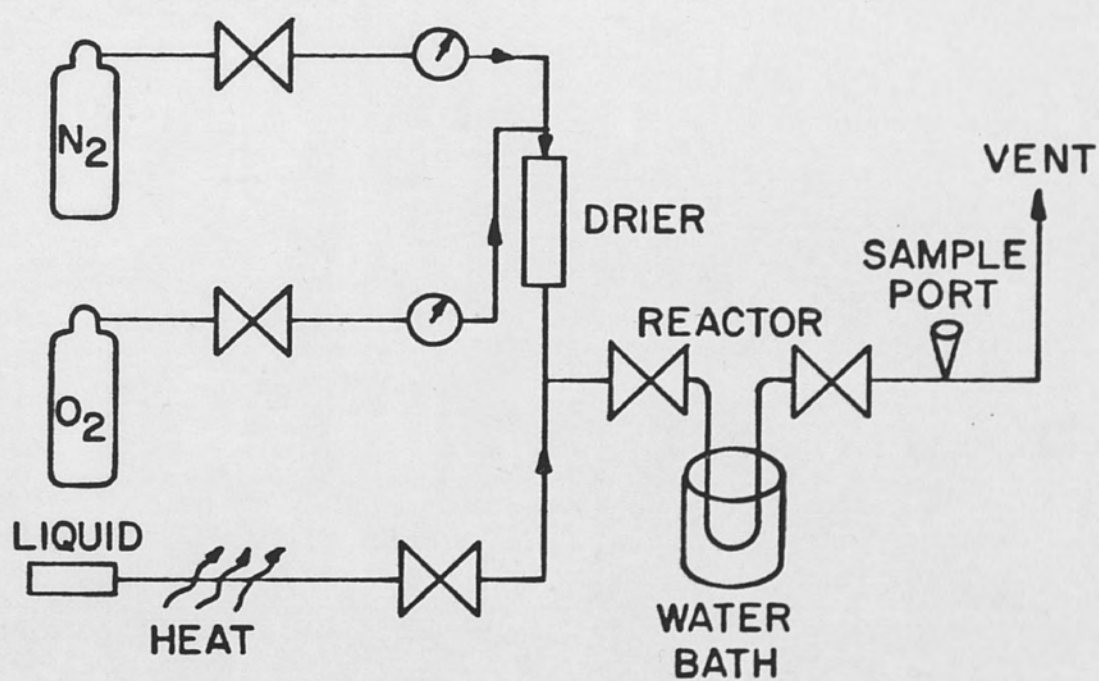


Figure 5. Experimental Schematic

100g of Al_2O_3 .¹² Based on these values 0.5g of NH_4ReO_4 per 1.92g of Al_2O_3 was used. A sample of 0.5g of the catalyst precursor was used for each run.

The ammonium perrheniate was converted to the active rhenium oxide by calcination methods. The catalyst precursor was added to the 0.1875 inch inside diameter glass tubing and placed in a sand bath. The sand bath temperature was controlled by twin iron resistor heaters, separately controlled with powerstat variable autotransformers. The powerstats were controlled manually and bath temperature was monitored with chromel-alumel thermocouples placed near the reactor.

The calcination was accomplished by maintaining a sand bath temperature of 550°C to 600°C for two hours while passing oxygen through the system at a gas flow of 55 cc/min. The sand bath temperature was maintained for an additional hour while nitrogen was passed through the reactor at a similar gas flow. The reactor was allowed to cool and the active catalyst was stored under nitrogen until needed.

The metathesis reaction was performed using a boiling water bath to hold the reactor temperature at 100°C. Dry nitrogen was used as a carrier gas with a flow of 25 cc/min. An autosyringe, model 355 (SAGE INSTRUMENTS), was used to deliver the required reactant into the reactor. The line passed through a boiling water bath to allow vaporization of the reactant mixture in order to maintain a gas phase catalytic reaction. The gas hourly space velocity for the reaction system was 3500 v/v.

Table 2 shows the autosyringe settings used for each reactant. The reactants were pumped in using a 10 ml syringe and a x 1/100 setting on the autosyringe. Each reactant was mixed in a 1:1 ratio by volume, with a nonreactive alkane having a similar volatility and molecular weight as an internal standard. Each stream was set up to deliver 20 ml/minute of gaseous reactant mixture. During the reaction run, a hot air gun was used to prevent condensation onto any of the glassware. Samples were drawn from the product stream during the course of the run. Each run lasted about five minutes,

TABLE 2
Autosyringe Settings for Reactants

<u>Reactant</u>	<u>MW</u> ²⁵	<u>d</u> ²⁵	<u>Liquid Flow (ml/min)</u>	<u>Syringe Setting %</u>
2-Pentene	70.14	0.6482	0.088	36.7
1,3-Pentadiene	68.13	0.6760	0.082	34.2
1,4-Pentadiene	68.13	0.6608	0.084	35.0
1-Hexene	84.16	0.6731	0.101	42.1
1,3-Hexadiene	82.15	0.7050	0.094	39.2
1,4-Hexadiene	82.15	0.7000	0.095	39.6
1,5-Hexadiene	82.15	0.6880	0.097	40.4
2,4-Hexadiene	82.15	0.7196	0.092	38.3

with the termination point being the point at which the catalyst bed had changed from its active offwhite color to its contaminated brown-black color.

Reactant and product analysis was performed using a H.P. model 5710A gas chromatograph (GC) in conjunction with a H.P. 3390A recorder integrator. The GC was run isothermally at 95°C with a helium carrier gas flow of 17 to 19 ml/min. The column used was a 20 ft. column of 22% (2-ethoxyethyl) sebacate and 8% (2-ethoxyethyl) adipate on chromosorb P. The products and reactants were identified either by comparison to pure compound GC retention times (Table 3) or by the homologous series determination of GC retention times. Every time the GC was used, it was calibrated based on a gaseous mixture of terminal alkenes (C_2-C_6) and by a gaseous mixture of alkanes (C_1-C_6) as needed. Figure 6 shows a typical extrapolated graph using the homologous series method for both alkenes and alkanes. This method was used to determine the length of the carbon chain of high molecular weight products, once the

TABLE 3
Retention Times of Olefin G.C. Standards

<u>Compound</u>	<u>R.T. (min)</u>
Ethylene	6.61
Propylene	7.23
1-Butene	8.17
2-Butene	8.59
1,3-Butadiene	9.25
1-Pentene	10.05
2-Pentene	11.17
1,3-Pentadiene	13.65
1,4-Pentadiene	13.58
Cyclopentene	13.11
1-Hexene	13.93
1,3-Hexadiene	15.85
1,4-Hexadiene	15.78
1,5-Hexadiene	15.72
2,4-Hexadiene	15.61

- Notes:
- 1) Retention times represent a helium gas flow of 17 cc/min and an oven temperature of 95°C.
 - 2) Column used was 20 ft. of 22% (2-ethoxyethyl) sebacate and 8% (2-ethoxyethyl) adipate on chromosorb P.

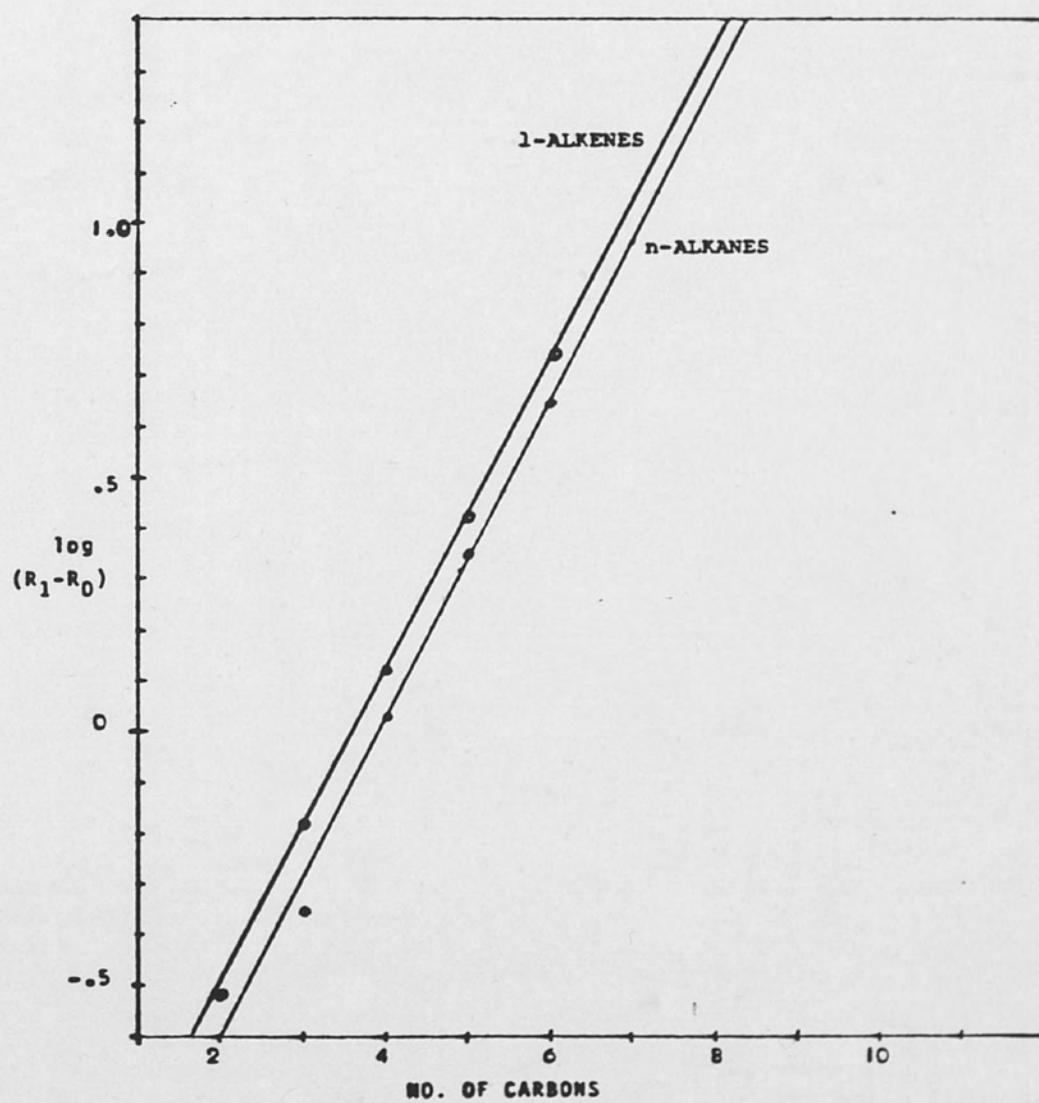


Figure 6. Typical Homologous Series Calibration

lower weight products had proven that metathesis did occur.

During the course of this study, high losses of reactant onto the catalyst had occurred. With this in mind, yields and conversions were based on products plus sampling of the catalyst bed. Catalyst samples were determined by warming the sample to allow vaporization of high molecular weight products, followed by GC analysis of the vapor.

RESULTS AND DISCUSSION

The experimental design was such that information was gathered on two questions. First the series of conjugated and nonconjugated dienes allowed the investigation of a reactivity difference between these systems. With the addition of cyclopentene to the reactant series, the metathesis reaction was also evaluated as a separation tool for the piperylene fraction.

Table 4 shows the experimental conversions and selectivities found during this study. The conversions were calculated based on sampling of entering and exiting streams. Catalyst bed sampling was used to help identify high molecular weight products. Selectivities were based on all metathesis products observed. Retention of reactant and product on the catalyst bed was calculated by means of material balances of entering and exiting streams. The high mass retention on the catalytic beds indicate a problem with obtaining high yields. However,

TABLE 4
Conversions and Selectivities of Reaction

<u>Reactant</u>	<u>Conversion (%)</u>	<u>Selectivity (%)</u>	<u>Loss on Catalyst (%)</u>
2-Pentene	53.7	66.3	33.7
1,3-Pentadiene	64.3	41.2	58.8
1,4-Pentadiene	14.1	81.2	18.8
Cyclopentene	0.9	82.7	17.3
1-Hexene	65.3	84.9	15.1
1,3-Hexadiene	89.3	51.9	48.1
1,4-Hexadiene	96.7	100.0	0.0
1,5-Hexadiene	62.8	50.0	50.0
2,4-Hexadiene	17.8	70.9	29.3

Notes: 1) All values include catalyst bed sampling.

2) Selectivities include any metathesis products.

Alkema¹⁵ indicated that yields can be greatly increased with the addition of hydrogen into the reactant stream.

The results of our study show no significant difference in conversion between the conjugated and nonconjugated diene systems. The postulate of lower energy levels of conjugated dienes was not verified. In fact, all dienes had significant reactivities. As a check, the entropy and enthalpy of formation were calculated by use of a Hewlett-Packard 9845B micro-computer and the ASTM CHETAH program.²⁶ The Gibb's energy of formation was then calculated. These results are displayed in Table 5. These results show no significant change in free energy of formation between conjugated and nonconjugated dienes and supports the experimental data.

The exception of this thermodynamic support was the low conversion of the cyclopentene. The calculated enthalpy of 7.21 kcal was mid-range of other values. The entropy of formation of cyclopentene was slightly lower than the other C-5 compounds. However, the lower entropy did not appear to be significant as it

TABLE 5

Calculated Values for Enthalpy, Entropy,
and Free Energy of Metathesis Reactants

<u>Reactant</u>	<u>H_f(kcal)</u>	<u>S_f(cal/K)</u>	<u>G_f(kcal)</u>
2-Pentene(Trans)	- 8.93	87.73	-41.7
1,3-Pentadiene(Trans)	17.70	82.53	-13.1
1,4-Pentadiene	24.37	82.95	-6.6
Cyclopentene	7.21	74.02	-27.6
1-Hexene	-11.46	98.83	-48.3
1,3-Hexadiene	12.36	92.27	-22.1
1,4-Hexadiene	16.35	95.57	-19.3
1,5-Hexadiene	18.90	92.90	-15.8
2,4-Hexadiene	9.36	90.24	-24.3

Notes: 1) All values are based on a reaction of water and carbon dioxide forming the olefin of interest.

2) All values are calculated at 100°C and 1 ATM. pressure, and for one mole of olefin.

detracts from the calculation of a Gibb's energy. The ASTM CHETAH²⁶ program was then used to gather thermodynamic data on the reaction systems. Instead of the energy of the reactant, the free energy of the reaction system was calculated. Each metathesis reaction was evaluated for possible products and the free energy of reaction then calculated at 100°C. Table 6 shows the results. All diene reactions had small Gibb's free energy changes. The cyclopentene reaction had a G of over 20 Kcal/gm. The large positive value indicates non-spontaneity and difficulty in forcing the metathesis reaction to proceed.

The thermodynamic data supported the experimentally observed results of a negligible reaction for metathesis of the cyclopentene. The combination of experimental and thermodynamic results suggests that the metathesis reaction may be used as a separation tool for the piperylene concentrate. The activated Re_2O_7 catalyst should have a selectivity such that the 1,3-pentadiene (54% of concentrate) reacts while the cyclopentene (25% of concen-

TABLE 6
Calculated Free Energy Changes
for Metatmesis Reactions

<u>Reactant</u>		<u>ΔG_{rx} (kcal)</u>
1,3-Pentadiene (Trans)	Ethylene + 2,4,6-Octatriene	0.36
	Propylene + 1,3,5-Heptatriene	-0.03
	2-Butene + 1,3,5-Hexatriene	1.77
	Butadiene + 2,4-Hexadiene	0.92
1,4-Pentadiene	Ethylene + 1,4,7-Octatriene	-0.53
Cyclopentene	1,6-Cyclodecadiene	20.47
1,3-Hexadiene	Ethylene + 3,5,7-Decatriene	-4.39
	Butadiene + 3,5-Octadiene	-2.20
1,4-Hexadiene	Ethylene + 2,5,8-Decatriene	-0.53
1,5-Hexadiene	Ethylene + 1,5,9-Decatriene	-0.53
2,4-Hexadiene	2-Butene + 2,4,6-Octatriene	0.37

Notes: 1) Free energies are calculated at 100°C and 1 ATM. pressure.

trate) passes through with minimal reaction. The products of the metathesis of piperylene should be olefins in the range of C_2-C_4 and C_6-C_8 . This difference in molecular weights should allow standard distillation techniques to be used to separate the metathesis products from the cyclopentene.

To test this theory, a reactant sample comprised of 50% 1,3-pentadiene, 25% cyclopentene, and 25% n-hexane was prepared. The reactant was passed through the catalyst bed as previously described. The results show that a metathesis reaction did occur. The results are presented in Table 7. The conversion and selectivity calculations follow in Figure 7.

A 51.7% conversion of 1,3-pentadiene, along with the obvious non-reactivity of cyclopentene confirms that the metathesis reaction can be used to separate the piperylene concentrate. As indicated, all possible metathesis reactions of 1,3-pentadiene did occur. However, the metathesis reaction to propylene (Table 6) gave the only spontaneous reaction for 1,3-pentadiene. Table 7 shows that prop-

1. Conversions

(a) of Piperylene $(1.168 - 0.564)/1.168 = 51.7\%$

(b) of Cyclopentene $(0.750 - 0.778)/0.750 = -3.7\%$

Negative conversions imply no reaction

2. Selectivity to Metathesis products

$$1 - (((1.168 - 0.564) - 0.3672)/(1.168 - 0.564)) = 60.8\%$$

3. Loss on catalyst 39.2%

Figure 7. Calculations for Piperylene - Cyclopentene Reaction

TABLE 7
Results of Piperylene - Cyclopentene Reaction

<u>Compound</u>	<u>Retention Times (min)</u>	<u>Reactant Smpl</u>	<u>Product Smpl</u>
Ethylene	6.66	---	0.008
Propylene	7.25	---	0.181
2-Butene	8.59	---	0.056
Butadiene	9.27	---	0.113
n-Hexane	12.30	1.0	1.0
Cyclopentene	13.11	0.750	0.778
Piperylene	13.65	1.168	0.564
1,3,5-Heptatriene	26.01	---	0.006

Notes: 1) Low M.W. products were confirmed by standard G.C. retention times.

2) Reactant was sampled from liquid.

3) Product was a gas sample at exit of reactor.

4) Reactant and product values are area calculations normalized to n-hexane.

ylene was in fact the highest yield product.

The catalyst bed was sampled in an attempt to identify high molecular weight products. Gas sampling showed many additional products (Table 8). Based on a homologous series calibration curve (Figure 8), the products were identified based on molecular weights. Using the low molecular weight products, metathesis was confirmed and high molecular weight product peaks were assumed to represent the remaining products.

Three sets of piperylene metathesis products were seen. Ethylene and octatriene, propylene and heptatriene, and butene and hexatriene were all detected in the catalyst sample. A significant amount of butadiene was seen in the product sample, but could not be confirmed in the catalyst bed sampling. No cyclodecadiene was observed in either sampling. With a negative conversion of cyclopentene, the implication of no reaction is strong.

Both questions were answered in this study. Experimental data backed by thermodynamic calculations were used to show that no

TABLE 8
Catalyst Bed Sample Analysis

<u>Compound</u>	<u>Retention Time (min)</u>	<u>Area %</u>
Ethylene	6.69	0.94
Propylene	7.27	12.76
2-Butene	8.62	8.45
n-Hexane	12.32	53.77
Cyclopentene	13.13	1.08
Piperylene	13.68	20.01
1,3,5-Hexatriene	16.70	0.24
1,3,5-Heptatriene	25.92	0.48
2,4,6-Octatriene	43.50	0.75

Notes: 1) 1.52% of total was found as impurities.

2) A large amount of cyclopentene and piperylene was lost on the catalyst bed.

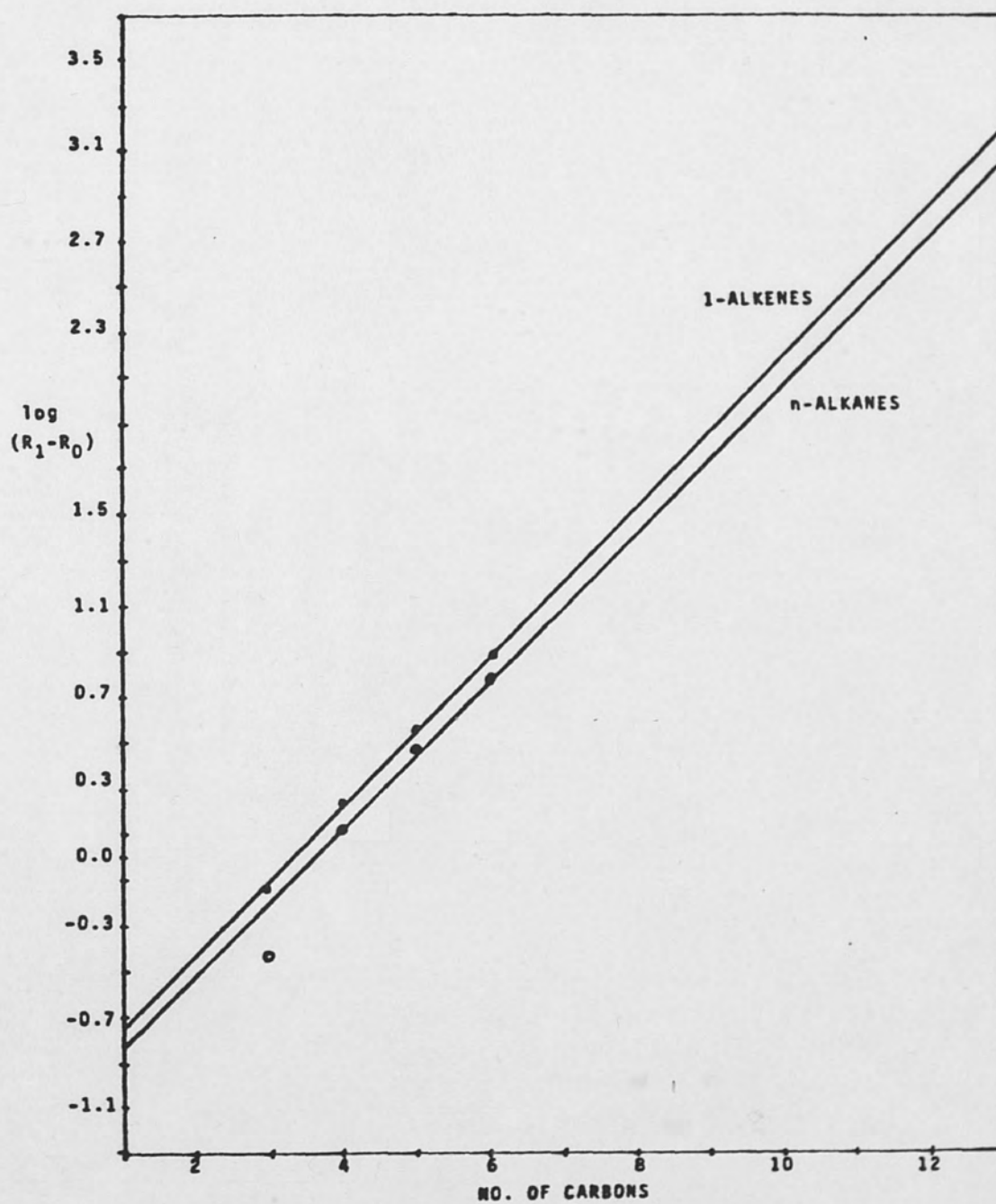


Figure 8. Homologous Series Calibration

reactivity difference is present between conjugated and nonconjugated diene systems. However, metathesis catalysis was shown to be a successful method of separating the major components of piperylene concentrate into more profitable products.

Recommendations

Additional work is needed to optimize catalyst life with the addition of hydrogen. Once this data has been gathered, a financial feasibility study may be conducted. Catalyst life is a key, along with regeneration methods. If these problems are solved, ethylene producers may be able to increase their profits with the use of catalytic metathesis reaction on the waste piperylene concentrate.

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