INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in “sectioning” the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.
PRICE, GEOFFREY LOYD
THE ACTIVE NATURE OF TELLURIUM LOADED ZEOLITE DEHYDROCYCLIZATION CATALYSTS.

RICE UNIVERSITY, PH.D., 1979
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark.

1. Glossy photographs
2. Colored illustrations
3. Photographs with dark background
4. Illustrations are poor copy
5. Print shows through as there is text on both sides of page
6. Indistinct, broken or small print on several pages throughout
7. Tightly bound copy with print lost in spine
8. Computer printout pages with indistinct print
9. Page(s) lacking when material received, and not available from school or author
10. Page(s) seem to be missing in numbering only as text follows
11. Poor carbon copy
12. Not original copy, several pages with blurred type
13. Appendix pages are poor copy
14. Original copy with light type
15. Curling and wrinkled pages
16. Other
RICE UNIVERSITY

THE ACTIVE NATURE OF TELLURIUM
LOADED ZEOLITE DEHYDROCYCLIZATION CATALYSTS

by

GEOFFREY L. PRICE

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTED:

Joe W. Hightower
G. W. Hightower, Professor
of Chemical Engineering
Chairman

L. V. McIntire, Professor
of Chemical Engineering

G. P. Glass, Associate
Professor of Chemistry

HOUSTON, TEXAS

MAY, 1979
ABSTRACT

THE ACTIVE NATURE OF TELLURIUM LOADED ZEOLITE DEHYDROCYCLIZATION CATALYSTS

by

Geoffrey L. Price

Due to the importance of dehydrocyclization reactions in industrial reforming operations to produce high octane gasolines, a study of tellurium loaded zeolite dehydrocyclization catalysts, discovered by Mobil researchers in 1970, has been made. Deuterium and $^{14}$C tracers, kinetic measurements, sodium NMR, ESCA, and hydrogen adsorption experiments have helped establish the active nature of this unusual catalyst.

The reactions of cyclohexane and n-hexane to form benzene have been studied kinetically, and in each case the reaction is first order in the respective reactant. Reaction products from the cyclohexane reaction are limited to benzene and very small amounts (less than two percent) of cyclohexene and cracking products. Products from the reaction of n-hexane are benzene, the n-hexenes, and 3-8 percent cracking products.
Deuterium tracer experiments with cyclohexane and cyclohexene along with kinetic measurements on the effect of hydrogen concentration on the reaction rate of cyclohexane indicate that the reaction of cyclohexane proceeds via a stepwise dehydrogenation of cyclohexane to yield benzene.

\(^{14}\text{C}\) tracer experiments have shown that the reaction of \(\text{n-hexane}\) proceeds only through the \(\text{n-hexenes}\) on the route to benzene.

Branched \(\text{C}_6\) reactions, \(\text{C}_8\) reactions, and \(\text{n-heptane}\) \(^{1-14}\text{C}\) experiments demonstrate that the tellurium loaded zeolite has essentially no activity for carbon skeletal rearrangement.

Sodium NMR and ESCA spectra indicate that the tellurium is coordinated to the cation associated with the support. Hydrogen adsorption measurements along with the ESCA results indicate that elemental tellurium, capable of adsorbing two hydrogen atoms per tellurium atom, is the active surface species.

A simple dehydrogenation mechanism, consistent with the observed kinetic and solid state work, probably is a simple step where two hydrogen atoms are simultaneously abstracted from the molecule.
ACKNOWLEDGEMENTS

I would like to express my sincere thanks to the following people and companies for their contribution to this work:

Professor Joe W. Hightower for serving as Thesis Director and for providing professional guidance and personal friendship throughout my graduate work.

Professors L. V. McIntire and G. P. Glass for serving on the oral committee.

National Science Foundation Grant Numbers GP-39482 and CHE-77-10541.

Welch Foundation for financial support.

Phillips Petroleum Company for providing financial support and chemicals.

Dr. Chuck Wagner of Shell Development for ESCA research work.

Dr. B. G. Silbernagel of Exxon for NMR research work.

Mobil Corporation for providing catalysts and financial support.

Dr. M. G. White, Dr. J. R. Hardee, Mr. Don Halcom, and Mr. Don Chickering, my co-workers, for providing helpful suggestions and many good times.

Mr. and Mrs. Jerry L. Price, my parents, and my brothers, Judson, Bradley and Wade, for their encouragement, guidance, and inspiration throughout my life.

TO THE GLORY OF GOD AND JESUS CHRIST,
MY PERSONAL SAVIOR
# TABLE OF CONTENTS

## I. Introduction

| Previous Work on Tellurium Loaded Zeolites            | 2 |
| Other Dehydrocyclization Catalysts                  | 7 |
| Chromia on Alumina Catalysts                        | 8 |
| Platinum and Related Catalysts                      | 11 |
| Thermodynamics                                      | 18 |
| Objectives                                          | 18 |

## II. Experimental

| Catalysts                                           | 21 |
| Chemicals                                           | 22 |
| Apparatus                                           | 23 |
| Gas Chromatograph                                   | 23 |
| Mass Spectrometer                                   | 29 |
| Liquid Scintillation Counter                        | 31 |
| NMR Spectrometer                                    | 31 |
| ESCA                                                | 31 |
| Recirculation Reactor System                        | 32 |
| Flow Reactor System                                 | 34 |

| Experimental Procedures                             | |
| Recirculation Experiments                            | 37 |
| Flow Reactor Experiments                             | 42 |
| Toluene Dealkylation                                 | 43 |
III. RESULTS

KINETIC MEASUREMENTS

Catalyst Aging
Cyclohexane Kinetics
Effect of Benzene
Effect of Hydrogen Concentration
n-Hexane Kinetics

OTHER REACTIONS

n-Heptane Reaction
C₈ Hydrocarbon Reactions
Branched C₆ Reactions

DEUTERIUM TRACER EXPERIMENTS

Cyclohexane with Deuterium
Cyclohexene with Deuterium
Benzene Deuterium Exchange
Methylcyclohexene Isomerization

RADIOACTIVE TRACER EXPERIMENTS

n-Hexane 1-¹⁴C Experiments
n-Heptane 1-¹⁴C Experiment

PHYSICAL MEASUREMENTS

Hydrogen Adsorption
ESCA
Sodium NMR

IV. DISCUSSION

KINETICS AND REACTION SCHEMES

Cyclohexane Reaction
n-Hexane Reaction
n-Heptane Reaction
Branched C₆ Reactions
C₈ Hydrocarbon Reactions
<p>| THE NATURE OF THE ACTIVE SITE | 109 |
| REACTION MECHANISMS | 112 |
| Dehydrogenation Mechanism | 112 |
| Olefin Deuterium Exchange Mechanism | 113 |
| Cyclohexene Disproportionation Mechanism | 114 |
| V. SUMMARY | 117 |
| REFERENCES | 120 |</p>
<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chromatograph Layout I</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Chromatograph Layout II</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Sample Chromatogram I</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Sample Chromatogram II</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Recirculation Reactor System</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>Flow Reactor System</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>Flow Reactor Experiment 1 with Cyclohexane</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>Flow Reactor Experiment 2 with Cyclohexane</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>Flow Reactor Experiment 3 with Cyclohexane</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>Linearized Rate Equation Plot for Cyclohexane</td>
<td>55</td>
</tr>
<tr>
<td>11</td>
<td>Activation Energy Plot for Cyclohexane</td>
<td>56</td>
</tr>
<tr>
<td>12</td>
<td>Flow Reactor Experiment 4 with Cyclohexane</td>
<td>58</td>
</tr>
<tr>
<td>13</td>
<td>Hydrogen Concentration Modelling for Cyclohexane Reaction</td>
<td>62</td>
</tr>
<tr>
<td>14</td>
<td>Effect of Hydrogen Concentration on the Reaction of Cyclohexane</td>
<td>63</td>
</tr>
<tr>
<td>15</td>
<td>Flow Reactor Experiment 1 with n-Hexane</td>
<td>65</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>16</td>
<td>Flow Reactor Modelling for n-Hexane Reaction</td>
<td>68</td>
</tr>
<tr>
<td>17</td>
<td>Flow Reactor Experiment 2 with n-Hexane</td>
<td>69</td>
</tr>
<tr>
<td>18</td>
<td>Flow Reactor Experiment 3 with n-Hexane</td>
<td>70</td>
</tr>
<tr>
<td>19</td>
<td>Activation Energy Plot 1 for n-Hexane Reaction</td>
<td>71</td>
</tr>
<tr>
<td>20</td>
<td>Activation Energy Plot 2 for n-Hexane Reaction</td>
<td>72</td>
</tr>
<tr>
<td>21</td>
<td>Flow Reactor Experiment with n-Heptane</td>
<td>73</td>
</tr>
<tr>
<td>22</td>
<td>Conversion Plot for Recirculation Experiment 1</td>
<td>76</td>
</tr>
<tr>
<td>23</td>
<td>Deuterium Incorporation for Recirculation Experiment 1</td>
<td>78</td>
</tr>
<tr>
<td>24</td>
<td>Mole Fraction Plot for Recirculation Experiment 2</td>
<td>80</td>
</tr>
<tr>
<td>25</td>
<td>Deuterium Incorporation for Recirculation Experiment 2</td>
<td>81</td>
</tr>
<tr>
<td>26</td>
<td>Selectivity Plot for Recirculation Experiment 2</td>
<td>83</td>
</tr>
<tr>
<td>27</td>
<td>Recirculation Experiment 3</td>
<td>85</td>
</tr>
<tr>
<td>28</td>
<td>Recirculation Experiment 4</td>
<td>86</td>
</tr>
<tr>
<td>29</td>
<td>Recirculation Experiment 5</td>
<td>87</td>
</tr>
<tr>
<td>30</td>
<td>Mole Fraction Plot for Recirculation Experiment 6</td>
<td>89</td>
</tr>
<tr>
<td>31</td>
<td>Specific Activity Plot for Recirculation Experiment 6</td>
<td>90</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>32</td>
<td>Mole Fraction Plot for Recirculation Experiment 7</td>
<td>93</td>
</tr>
<tr>
<td>33</td>
<td>Specific Activity Plot for Recirculation Experiment 7</td>
<td>94</td>
</tr>
<tr>
<td>34</td>
<td>Hydrogen Isobar</td>
<td>96</td>
</tr>
<tr>
<td>35</td>
<td>NMR Results</td>
<td>100</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermodynamic Properties</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>Syringe Pump Data</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>Parameters and Symbols for Figure 10</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>Product Distributions from Various Reactants</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>ESCA Results</td>
<td>98</td>
</tr>
</tbody>
</table>
I - INTRODUCTION

Dehydrocyclization is an important reaction in the catalytic reforming of napthas to make high octane gasolines. Reforming operations account for roughly 40 to 50 percent of the total gasoline produced. The need for additional reforming capacity has been steadily increasing over the past few years due particularly to the increased demand for high octane unleaded gasolines.

Haensel of Universal Oil Products conducted pioneering research work into the industrial use of platinum reforming catalysts. His patent (1) on platinum supported on halogenated alumina opened the doors for industrial application of such catalysts in the late 1950's and early 1960's. Probably the most widely used industrial reforming catalyst today is platinum on chlorided alumina. Platinum/rhenium on chlorided alumina is also used extensively because of its high stability. However, the major drawback of Pt/Re catalysts is that the addition of rhenium decreases the ability of platinum to perform cyclization. Other bimetallic and multimetallic catalysts (e.g. Exxon's KX-130 which contains platinum and iridium on alumina) have also increased in popularity.
Chromia catalysts have been widely studied as dehydrocyclization catalysts but have not been used industrially because they polymerize C₅ ring compounds which leads to coke formation and a corresponding loss of catalytic activity. C₅ ring compounds account for as much as 30 percent of the hydrocarbons in natural and hydrocracked napthas. Platinum catalysts, on the other hand, have the ability to expand C₅ to C₆ rings and thus produce aromatic products.

This work deals with tellurium loaded zeolite dehydrocyclization catalysts. Although these catalysts have never been used industrially, they are attractive because they give high selectivities to aromatic versus cracked products. Platinum reforming catalysts produce reasonable quantities of aromatic products along with isomerized paraffins. However, if the conditions are adjusted to optimize aromatic products, a sacrifice to large quantities of cracking products is simultaneously made.

PREVIOUS WORK ON TELLURIUM LOADED ZEOLITES

The dehydrocyclization activity of tellurium loaded zeolites was discovered by Maile and Weisz (2) in 1970. They were investigating the n-hexane cracking properties of sulfur loaded zeolites (i.e., zeolites impregnated or mixed with sulfur) when they stumbled upon the unusual
behavior of the tellurium loaded zeolites. After some work with sulfur loaded zeolites, they tried selenium loaded zeolites which yielded cracking activities similar to the sulfur loaded zeolites. But when they took one more step down the periodic table and loaded the zeolite with tellurium, instead of cracking products from n-hexane, they found a high yield of benzene. Co-workers of Maile and Weisz at Mobil Research and Development in Princeton, New Jersey continued work on the tellurium loaded zeolites.

Lang et al. (3) investigated the effects of catalyst preparation techniques on the selectivity and stability of tellurium loaded on various supports. They studied the effects of activation procedure, method of tellurium addition, supports, source of tellurium, and the tellurium content. Their standard reaction was n-hexane in hydrogen carrier gas reacted at 538°C and one atmosphere total pressure. Benzene and cracking products were observed and selectivities were reported as selectivities to benzene.

The researchers found that activation of the catalyst in flowing hydrogen around 538°C produces more active catalysts than those treated in air. Also, they found dry ball-milling the tellurium source (elemental tellurium or metal tellurides) for 2-5 hours with the support produces better catalysts than catalysts prepared by tellurium salt impregnation of the support. Many types of zeolite supports were tried, but zeolites with a low silica to alumina ratio
(i.e., X-type zeolites) containing alkali metals (Na, K, Rb, or Ce) gave much more selective catalysts than zeolites containing alkaline earth metals (Mg, Ca, or Ba) or Y-type zeolites. Alumina supports yielded very poor catalysts even if they were promoted with sodium.

The researchers found that many metal tellurides such as ZrTe$_2$, Cr$_2$Te$_3$, and TaTe$_2$ when used as the tellurium source gave excellent catalysts, but they speculated that the hydrogen activation simply reduces the tellurides to elemental tellurium. Elemental tellurium used as the tellurium source gave catalysts of similar quality as those made with metal tellurides. Tellurium loadings in the range 3 to 8 percent by weight gave the highest selectivities and the best catalyst stability.

In summary, the researchers found that the most selective and stable catalysts are prepared by dry ball-milling 3 to 8 weight percent elemental tellurium with NaX, KX, RbX, or CeX zeolite for 2-5 hours and activating it in flowing hydrogen around 538°C. Selectivities of roughly 90-95 percent were achieved with catalysts of this type.

From their results, the workers concluded that the cations associated with the zeolite support are necessary for producing an active catalyst by coordination of the metal with tellurium.
Mikovsky et al. (4) continued work on tellurium loaded zeolites by attempting to identify the nature of the active site. They found that hydrogen slowly eluted tellurium from Te/NaX until an asymptotic value of about 3.5 percent tellurium is reached. But tellurium was eluted from Te/KX at a much slower rate than from Te/NaX. They also discovered that helium would slowly elute tellurium from Te/NaX until all the tellurium is eventually gone. They concluded that hydrogen is necessary for the stability of the cation-tellurium coordination. In further studies, the researchers found that although Te/NaX produces more active catalysts than Te/KX, Te/KX is more selective to benzene than Te/NaX.

Citing the X-ray crystallographic work of Olson et al. (5), Mikovsky et al. (4) concluded that the active species is a Te\(^{\text{-2}}\) ion nested in the supercage of the NaX zeolite between Site II and Site III sodium atoms. They backed up their conclusion by showing that catalysts of low Site III sodium content show little activity. They further reported that the slight cracking activity of the catalyst is due to H\(^{\text{+}}\) ions produced in the reduction of Te\(^{\text{0}}\) to Te\(^{\text{-2}}\).

Olson et al. (5) did diffuse reflectance and hydrogen sorption experiments along with their careful X-ray crystallographic work and these measurements support the theory that H\(^{\text{+}}\) ions are on the catalyst surface after the
reduction of the tellurium. However, the authors did not consider the fact that Te/KX has a lower overall activity but higher benzene selectivity than Te/NaX. According to their model, Te/KX should have the same cracking activity as the Te/NaX. Since Te/KX has an overall activity lower than Te/NaX, the selectivity to benzene for Te/KX should be lower than Te/NaX. A better solid-state study of Te/NaX, however, does not at present exist.

Silvestri and Smith (6) investigated the effect of hydrogen partial pressure on the rate of the n-hexane reaction. They compared the Te/NaX result with similar data that they obtained from a chromia-alumina catalyst. Using the reaction scheme reported by Kazansky et al. (7) for the n-hexane reaction over chromia, Silvestri and Smith produced a mathematical interpretation of the reaction scheme that is consistent with the observed effect of hydrogen partial pressure for both chromia-alumina and Te/NaX catalysts. They concluded that the reaction scheme was probably similar for both catalysts. The reaction scheme reported by Kazansky et al. (7) is:

\[
\begin{align*}
\text{hexane} & \rightarrow \text{hexenes} + H_2 \\
\text{hexenes} & \rightarrow \text{hexadienes} + H_2 \\
\text{hexadienes} & \rightarrow \text{hexatrienes} + H_2 \\
\text{hexatrienes} & \rightarrow \text{cyclohexadienes (non-catalytic)} \\
\text{cyclohexadienes} & \rightarrow \text{benzene} + H_2
\end{align*}
\]

Reaction Scheme I
OTHER DEHYDROCYCLIZATION CATALYSIS

It seems appropriate to examine other catalysts which promote dehydrocyclization, particularly aromatization, of hydrocarbons so that similarities and dissimilarities with tellurium loaded zeolites might be realized. Let me make a few general observations for the moment and make specific references later in the text.

Many metals such as Pt, Pd, Ni, Rh, Cr, and others promote aromatization of hydrocarbons under the proper conditions. The most widely studied aromatization catalysts are those containing platinum and related metals and those containing chromium. The reaction products from platinum and related metals are so widely different from the chromium containing catalysts that separate consideration is warranted.

Furthermore, many reaction mechanisms have been proposed for these catalysts. Most researchers agree upon the reaction mechanisms over chromia catalysts although some questions remain unanswered. But a widely accepted reaction mechanism for platinum and related catalysts does not at present exist. Part of the disagreement on the reaction mechanism appears to be due to differences in supports and preparation techniques for the catalysts. Thus, catalysts prepared in different manners will generally be considered separately though some authors have
attempted to resolve the discrepancies by investigating catalysts prepared in different manners.

**Chromia on Alumina Catalysts**

Russian workers (7,8,9) have done extensive work with the reaction scheme of the aromatization of paraffins over chromia on alumina promoted with potassia. Kazansky et al. (7) have used radioactive tracers to show that the cyclization step in the aromatization of n-hexane occurs via hexatriene reacting to form cyclohexadiene. Lewis and Steiner (10) showed that hexatrienes react thermally even below 200°C to form cyclohexadiene. Kazansky et al. (7) then concluded that the cyclization step is not catalytic since the reaction of n-hexane was run in the range of 530°C. They reported Reaction Scheme I (see page 6) as the scheme for the n-hexane reaction. They further concluded that chromia on alumina catalysts have no activity for ring closure and are simply dehydrogenation catalysts.

Zhorov et al. (8) reported that the activation energy for dehydrogenation of paraffins to olefins is 40 Kcal/mole, for cracking of paraffins is 45 Kcal/mole, and for the overall aromatization of paraffins over chromia on alumina catalysts is 30 Kcal/mole. They further reported that the activation energies are almost independent of the molecular weight of the paraffin. Panchenko et al. (9)
reported that the dehydrogenation of paraffins to olefins is the rate limiting step in the aromatization of paraffins and is 7 to 8 times slower than olefins reacting to aromatics over chromia on alumina. They further reported that the activation energy for dehydrogenation of olefins to paraffins is 39 Kcal/mole and for the overall aromatization of paraffins is 48 Kcal/mole.

But the reaction of paraffins over chromia catalysts may not be as simple as it appears. Mitchell (11) showed that in the aromatization of n-heptane $^{14}$C over chromia on alumina catalysts, less than 30 percent of the $^{14}$C is found in the side chain of the toluene product. A simple C$_6$ ring closure of say heptatriene would yield 50 percent of the $^{14}$C in the methyl group. Chen et al. (12) did similar $^{14}$C labeling experiments over pure chromia, chromia on acidic alumina, and chromia on non-acidic alumina. They found that the radioactive content of the side chain is different over each catalyst. The side chain radioactivity ranged from a low of 17.5 percent for chromia on non-acidic alumina to 47.4 percent on the pure chromia catalyst. The authors proposed that C$_6$ and C$_7$ ring closures are competing in the production of toluene. C$_7$ ring closure followed by statistical rearrangement to a C$_6$ ring would yield 14.3 percent radioactivity in the side chain. This suggests that the acidity of the support influences C$_6$ or C$_7$ ring
closure. Bremer et al. (13) have done additional work on the effect of catalyst preparation on the reaction of paraffins over chromia catalysts.

Chromia catalysts also have the ability to perform skeletal rearrangement of hydrocarbons. Cannings et al. (14) have reported that 2,2,4-trimethylpentane yields p-xylene over chromia on alumina. They report that the rearrangement occurs via bond shift from carbon 3 to one of the methyl groups in the 2 position followed by ring closure. Davis (15) has reported the aromatic product distribution over chromia on alumina from a variety of hydrocarbons containing a quaternary carbon. Xylenes were the major products reported from the reaction of 2,2-dimethylhexane and 3,3-dimethylhexane indicating that carbon skeletal rearrangement must take place at some step in the reaction. However, no authors have reported rearranged paraffins as reaction products. Rearrangement of olefinic intermediates over acidic sites on the support or even thermal rearrangement is possible. Rearrangement of intermediates could also explain the results of the radioactive experiments performed by Mitchell (11) and Chen et al. (12).

In summary, the dehydrocyclization of n-hexane probably occurs via Reaction Scheme I (see page 6). But the skeletal rearrangements of hydrocarbons over chromia are not well understood. The catalyst preparation technique
apparently influences the reaction mechanism involved in the conversion of paraffins to aromatic products.

**Platinum and Related Catalysts**

The study of dehydrocyclization of paraffins over platinum and related catalysts is complicated due to the fact that these catalysts in general promote other side reactions. Though many types of reactions such as hydrogenolysis (cracking), hydrogenation, carbon skeletal isomerization, dehydrocyclization, and deuterium exchange have been studied over catalysts of this type, we will try to limit our discussion to dehydrocyclization reactions.

In the study of dehydrocyclization reactions over platinum and related catalysts, the mechanisms by which the C₆ ring (which eventually becomes the aromatic ring) is formed is not well agreed upon.

Two fundamental theories are argued in the literature. Some authors claim direct C₆ ring closure and others claim C₅ ring closure followed by ring expansion yields the aromatic ring. It appears that catalyst preparation techniques influence which mechanism predominates but the reason for the activity changes from one catalyst to another has not been well established.

DeJongste et al. (16) have studied the n-hexane reaction over Pt/Cu and Pt/Au alloys. They determined that increasing the copper content of the Pt/Cu catalyst
increases the selectivity of n-hexane to benzene with a corresponding decrease in hydrogenolysis and skeletal rearrangement. The authors further reported the apparent activation energies of the various processes as a function of platinum content. The activation energies reported for the skeletal rearrangement rate, overall reaction rate, and hydrogenolysis rate remained essentially constant with platinum content at 60, 40, and 35 Kcal/mole, respectively. However, the apparent activation energy for aromatization to benzene dropped from about 40 Kcal/mole at 1 percent platinum content to about 20 Kcal/mole at 100 percent platinum content. The Pt/Au alloy showed almost no hydrogenolysis activity and gave mainly skeletal rearrangement products. The authors contended that methylcyclopentane is the precursor to benzene. They believed that methylcyclopentane (which they detected in appreciable quantities in the products) is formed via an \( \alpha,\alpha,(\alpha-1) \) tri-absorbed species on the surface. They also argued that copper blocks the non-selective ring opening of methylcyclopentane thus increasing the possibility of \( \text{C}_5 \) to \( \text{C}_6 \) ring expansion and a corresponding increase in benzene selectivity.

Donniss (17) studied the reaction of methylcyclopentane over a commercial Pt-Al\(_2\)O\(_3\)-Cl reforming catalyst. He concluded that ring expansion of methylcyclopentane to give cyclohexane (and eventually benzene) occurs over the acidic sites of the support. He also suggested that the
selective ring opening of methylcyclopentane to give a linear C$_6$ chain occurs over the same acidic sites. But he presents evidence that the ring opening to form 2- or 3-methylpentane occurs over platinum sites. All hydrogenations and dehydrogenations were shown to occur over the platinum sites.

Note that there is a basic disagreement between the papers by de Jongste et al. (16) and Donnis (17). Presumably the Pt/Cu alloy used by de Jongste et al. (16) has no acidic sites, but they reported that methylcyclopentane ring expansion is responsible for the formation of benzene. But Donnis (17) claims that acidic sites are required for the C$_5$ ring expansion over his catalyst. This disagreement is perplexing and must be due to a difference in the platinum properties due to the catalyst preparation techniques. This type of disagreement abounds in the literature and it seems redundant to dwell on it further.

Dautzenberg and Platteeuw (18) used a non-acidic alumina support for platinum to study the reaction of several different hydrocarbons. Benzene was a primary product from the reaction of n-hexane but was a secondary product from the reaction of 2-methylpentane. Methylocyclopentane was a primary product in both reactions. They concluded that benzene is formed via direct C$_6$ ring closure or via Reaction Scheme I (see page 6) as reported by Kazansky et al. (7). They also studied the aromatic
distribution obtained from 2,5-dimethylhexane, 2,2,4-trimethylpentane, 1,1,3-trimethylcyclopentane, isopropylcyclopentane, and 1,1-dimethylcyclohexane. The highest conversions to aromatics were obtained with 2,5-dimethylhexane and 1,1-dimethylcyclohexane. The major products were those expected if the carbon skeletal structure was not rearranged. The major products obtained from the other compounds were those expected from a single bond shift. They also found that the catalyst selectivity is not affected by the platinum particle size in the range 15 to 50 angstroms. In a later paper, Dautzenberg and Platteeuw (19) extended their work to include platinum levels up to 10 percent.

Barron et al. (20) reported that 2,3-dimethylbutane is very slowly isomerized to methylpentanes and cracked extensively over 0.2 percent platinum on alumina. They further reported that 3-methylpentane reaches essentially equilibrium with 2-methylpentane and n-hexane at 340°C. The alumina support itself was shown not to promote skeletal rearrangement or hydrogenolysis. From the reaction of 1,1,2-trimethylcyclopentane, the researchers reported 19 percent toluene, 53 percent m-xylene, 28 percent p-xylene, and no o-xylene in the aromatic products. Note that m-xylene or o-xylene are the expected aromatic products from C_5 ring expansion. Barron et al. (20) proposed a
tri-adsorbed species intermediate to explain their results. They concluded that platinum is not simply a hydrogenation/dehydrogenation agent.

Ponec and Sachtler (21) reported activation energies in the range of 44-57 Kcal/mole for the reaction of n-hexane over Ni/Cu alloys. They found that the selectivity to benzene and \( C_6 \) isomerization products increases with increasing copper content of the catalyst. Over pure Ni, hydrogenolysis is the sole reaction of n-hexane.

Muller and Gault (22) reported that the reactions of 2,3-dimethylbutane and 2,2-dimethylbutane yield significant quantities of 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, and benzene over platinum films. Surprisingly, benzene was the major \( C_6 \) product obtained from 2,2-dimethylbutane at 350°C. With the aid of \(^{13}\)C labeling experiments, the authors concluded that skeletal rearrangements consist of multiple bond shifts and \( C_5 \) ring closures and openings. These multiple shifts are realized even though overall conversions are about 1 percent. This indicates that the multiple shifts occur during a single absorption of the molecule. Roughly 40 to 60 percent cracking products were simultaneously reported.

Callendar et al. (23) have proposed that aromatization of paraffins over 0.1 to 1 percent platinum on acidic alumina occurs via ring expansion of alkylcyclopentane intermediates and direct \( C_6 \) ring closure. They
propose that the platinum and the alumina support function independently of one another. They concluded that the platinum functions as a hydrogenation/dehydrogenation site and that the acidic sites are responsible for C₅ ring expansion and C₅ ring closure of olefins. The authors believe that C₅ ring closure of olefins over acidic sites occurs via a carbonium ion. They reported that alkylcyclopentanes were intermediates for both branched paraffins and aromatic products. They further reported that the platinum particle size influences the rate of paraffin cyclization.

Fogelberg et al. (24) reported that the major aromatic products produced from the reactions of methylheptanes and n-octane are those predicted by direct C₆ ring closure without skeletal rearrangement over platinum on alumina catalysts.

Davis (15) has studied the reactions of cyclic and non-cyclic paraffins which contain a quaternary carbon over platinum on non-acidic alumina and compared the results with similar experiments performed on a chromia on alumina catalyst. He concluded that aromatization occurred via direct C₆ ring closure for the non-cyclic paraffins for both catalysts. He also concluded that chromia on alumina has a higher activity for skeletal rearrangement of the cyclic paraffins than platinum on alumina. Davis (15) also reports the aromatic product distributions obtained
from 1,1,3-trimethylcyclohexane over palladium on non-acidic alumina and rhodium on non-acidic alumina. The rhodium catalyst gave results similar to the chromia and the platinum catalysts where m-xylene produced via demethylation was the major product. But the major product obtained from the palladium catalyst was 1,2,4-trimethylbenzene. The palladium catalyst therefore appears to have the highest activity for skeletal rearrangement.

Finally, an excellent paper has been written by Chambellan et al. (25) in which the authors try to explain the various catalytic properties of platinum on alumina catalysts. They studied the isomerization of $^{13}$C labeled hexanes over 0.05 to 0.7 percent platinum on alumina. From their results, they proposed a model which attempts to explain how crystallite size affects the selectivity and the rate of platinum catalyzed reactions. They proposed that a reaction takes place by 1) weak adsorption on a face of the crystallite, 2) superficial migration of the adsorbed molecule to a reactive site, 3) formation of a highly dehydrogenated species, and 4) skeletal rearrangement of the strongly adsorbed species. The authors further explained how different types of crystallite faces are formed by different types of catalyst preparation techniques and how the different crystallite faces have different activities.
THERMODYNAMICS

Thermodynamics must always be considered when dealing with chemical reactions. A complete thermodynamic picture of all the reactions presented in this work, however, would be tedious and not of great value. Enthalpies of reaction and thermodynamic equilibrium constants for some of the reactions are presented in Table 1. The data used to obtain the information in the table were taken from API Project 44 except for the cyclohexene properties which were estimated by standard engineering techniques. Note that in some of the reactions, multiple products are possible but approximate values reflecting the overall reaction characteristics are presented. Basically, one can see that aromatization of paraffins involves highly endothermic reactions which are thermodynamically very favorable at moderate to low pressures (near one atmosphere) in the temperature range of interest (near 800°K).

OBJECTIVES

The purpose of this study was to identify the types of reactions that tellurium loaded zeolites will catalyze. Furthermore, we wished to determine reaction pathways, kinetic parameters, and reaction mechanisms of some of these reactions. A third part of the study was to provide
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_R$ (Kcal/mole)</th>
<th>$K$ (Thermodynamic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane $\rightarrow$ benzene + 4 H$_2$</td>
<td>64</td>
<td>$3.7 \times 10^5$</td>
</tr>
<tr>
<td>n-heptane $\rightarrow$ toluene + 4 H$_2$</td>
<td>60</td>
<td>$9.0 \times 10^6$</td>
</tr>
<tr>
<td>n-octane $\rightarrow$ C$_8$ aromatics + 4 H$_2$</td>
<td>60</td>
<td>$1.2 \times 10^7$</td>
</tr>
<tr>
<td>cyclohexane $\rightarrow$ benzene + 3 H$_2$</td>
<td>53</td>
<td>$2.1 \times 10^6$</td>
</tr>
<tr>
<td>n-hexane $\rightarrow$ n-hexenes + H$_2$</td>
<td>29</td>
<td>0.2</td>
</tr>
<tr>
<td>cyclohexane $\rightarrow$ cyclohexene + H$_2$</td>
<td>29</td>
<td>0.08</td>
</tr>
</tbody>
</table>

All values reported at 800°K, components in the ideal gas state.
information about the chemical nature of the catalytically active sites. In this thesis work, we have achieved some of the objectives, although additional research must be undertaken to establish completely the details of this fascinating catalytic system.
II - EXPERIMENTAL

CATALYSTS

The support used throughout this work was a Linde 13X molecular sieve. The molecular sieve contained 15.1 percent sodium and had a silicon to aluminum mole ratio of 1.3. The surface area as reported by Lang et al. (2) was 606 m²/g.

The tellurium was a fine powder donated by Mobil Corporation and was originally obtained from Matheson, Coleman and Bell. The tellurium assayed 99.5 percent.

The catalyst used for most of the work was prepared by Mobil researchers in Princeton, New Jersey. The catalyst was prepared by taking 11 percent tellurium by weight and ball-milling it with the 13X zeolite for 4 hours. A catalyst prepared in exactly the same manner in our laboratory was used for some of the recirculation reactions and for NMR studies. The two catalysts showed very similar activity.

All catalysts used for reactions were pelletized, ground, and sieved to 40/60 mesh except for catalysts used for diffusional effects studies. Catalysts used for ESCA and NMR were in their powdered form.
CHEMICALS

The following chemicals were kindly donated by the Phillips Petroleum Company:

n-hexane, 99.99 mole percent
2-methylpentane, 99+ mole percent
methylcyclopentane, 99+ mole percent
1-hexene, 99+ mole percent
cis-2-hexene, 99.21 mole percent
cyclohexane, 99.5 mole percent
benzene, 99+ mole percent
n-heptane, 99+ mole percent
n-octane, 99+ mole percent

The following chemicals were purchased from Chemical Samples Company:

1,1-Dimethylcyclohexane, 98 percent
cis-1,2-Dimethylcyclohexane, 99.8 percent
trans-1,2-Dimethylcyclohexane, 99.7 percent
trans-1,3-Dimethylcyclohexane, 99 percent
cyclohexene, 99.8 percent
1,3-cyclohexadiene, 99 percent

n-Hexane \(^{14}C\) and n-heptane \(^{14}C\) were obtained from American Radiochemical Company. Their specific activity before dilution was 1 millicurie/millimole. The
n-hexane $^{14}$C was diluted approximately 50 to 1 with pure n-hexane and the n-heptane $^{14}$C was diluted approximately 10 to 1 with pure n-heptane before use.

Deuterium was produced by electrolysis of $D_2O$ in an Elhygen palladium diffusion deuterium generator. The $D_2O$ used in the deuterium generator was made by Aldrich and had an isotopic purity of 99.8 percent. The deuterium gas was analyzed by mass spectrometry and showed an isotopic purity of 99.5 percent.

Hydrogen was ultrahigh purity grade (99.995 percent) obtained from Matheson.

Helium used for gas chromatography was zero grade obtained from Liquid Carbonic.

All chemicals used for toluene dealkylation were standard ACS reagent grade chemicals.

APPARATUS

Gas Chromatograph

The gas chromatograph used throughout this work was "homemade." The detector was a Gow-Mac microvolume thermal conductivity cell with four rhenium-tungsten elements operated at a bridge current of 100 ma. The bridge power supply was also "homemade." The detector was emersed in a Dewar flask filled with vermiculite and thermostatted at $150^\circ$C.
A Varian electronic integrator was used to determine peak areas and a Leeds and Northrup strip chart recorder recorded the chromatogram.

Chromatograph columns were emersed in Dewar flasks. The flasks were filled with water for column temperatures of up to 100°C or with vermiculite for higher temperatures. Variacs were used to control nichrome heaters as required to attain column temperatures.

Two chromatograph layouts are shown in Figures 1 and 2. Figure 1 gives the general layout used for almost all the analyses. Samples coming from the sample loop (see Flow Reactor section) were separated on either of two columns selected by three-way switching valves V1 and V2. A heated injection port was used to determine retention times and response factors of liquid standards. Many different columns were used depending on the application. Columns and their applications are listed below.

1) 3/16" O.D. x 15' 20% Carbowax 20M on 60/80 mesh Chromasorb W at 120°C.

Separation of cyclohexane, cyclohexene, cyclohexadienes, and benzene. Figure 3 shows a typical separation of cyclohexane reaction products obtained with this column.

Separation of n-heptane, benzene, and toluene.
FIGURE 3. Sample Chromatogram I
2) 3/16" O.D. x 30' 20% Carbowax 20M on 60/80 mesh Chromasorb W at 120°C.

Separation of n-hexane, n-hexenes (as one peak), and benzene. (Non-radioactive samples only.)

3) 3/16" O.D. x 15' 3% Bentone 34, 3% diisodecylphthalate on 60/80 mesh Chromasorb W at 130°C.

Separation of benzene+n-octane (eluted as one peak), toluene, o-, m-, and p-xylene, and ethylbenzene.
Separation of any dimethylocyclohexane from toluene, o-, m-, and p-xylene, and ethylbenzene.

4) 1/4" O.D. x 5' 10% SE-30 on 60/80 mesh Chromasorb W at 100°C.

Separation of benzene and n-octane (used in conjunction with column 3).

5) 3/8" O.D. x 7' 10% SE-30 on 60/80 mesh Chromasorb W at 120°C.

Used for purification of large quantities of toluene by separation of toluene from benzene and n-heptane.

Figure 2 shows the chromatograph layout for the analysis of radioactive n-hexane experiments. Hexane and hexenes eluting from column 1 (3/16" O.D. x 15' 20% Carbowax 20M on 60/80 mesh Chromasorb W at 120°C) were allowed to flow into column 2 (1/4" O.D. x 5' 20% propylene carbonate on 60/80 mesh Chromasorb W at 25°C) where they were separated, detected and collected at port 1. n-Hexane was completely resolved from the n-hexanes and the n-hexenes
were resolved into two peaks. The n-hexenes were collected, however, in a single sample vial.

After the hexane and hexenes were detected, the bridge polarity was switched, the trap was cooled with liquid nitrogen, and benzene was eluted from column 1. The benzene was detected and collected in the trap. The benzene was not allowed to reach column 2 because it had an extremely long retention time on column 2. Once the analysis was complete, V1 was switched, the trap was thawed, and the benzene was collected at port 2. A sample chromatogram is shown in Figure 4.

**Mass Spectrometer**

The mass spectrometer used in deuterium exchange reaction was a Consolidated Electrodyamics Corporation model 21-104. The nominal ionizing voltage was set at 5 volts to minimize fragmentation of the molecules. The mass spectrometer was operated in a slow scan mode so that peaks were recorded on a Leeds and Northrup strip chart recorder. Samples were expanded from glass sample tubes into a vacuum inlet system to provide a sample pressure of approximately 100 microns. The sample passed through a gold leak seal into the analyser at a pressure of approximately $10^{-6}$ torr. Background pressure in the analyser was approximately $5 \times 10^{-8}$ torr.
FIGURE 4. Sample Chromatogram II
Liquid Scintillation Counter

A Unilux I liquid scintillation counter made by Nuclear-Chicago was used for all radioactive counting. The counter was operated at room temperature. Samples were automatically changed by the counter and the counter could accommodate up to 100 samples. Counting time for each sample was selected to be 40 minutes.

NMR Spectrometer

The NMR spectroscopy results were kindly obtained by B. G. Silbernagel at the Exxon Corporate Research Center in Linden, New Jersey. The NMR was a Varian model WL-112 wide-line NMR with a 12" Varian magnet. The radio frequency source was supplied by a General Radio frequency synthesizer which operated from 3-35 megahertz. The magnetic field was oscillated sinusoidally at 35 hertz.

ESCA

ESCA spectra were kindly taken by Chuck Wagner at Shell Development-West Hollow in Houston, Texas. The Varian IEE instrument was equipped with a high intensity aluminum X-ray anode operated at 10 KV and 100 ma. The analyser pressure was between $2 \times 10^{-6}$ and $5 \times 10^{-6}$ torr. Samples were prepared by treating them in flowing hydrogen for 12 hours at 500°C, cooling them to room temperature in
hydrogen and sealing them in a reactor similar to the reactors used in the recirculation system. The samples were opened at Shell in a nitrogen glovebox and transferred into the instrument without ever being exposed to air.

**Recirculation Reactor System**

Radioactive tracer and deuterium exchange reactions were run on the recirculation reactor system shown in Figure 5.

Vacuum for the system was provided by a mercury diffusion pump backed by a mechanical pump. Pressures below $10^{-6}$ torr could be routinely reached. Vacuum was measured by a mercury McLeod gauge.

Reactants were admitted into and samples were withdrawn from the system through ground glass joint J1. Mercury manometer M1 was used to measure pressures of reactants. Stopcock S1 was opened occasionally to provide a reference vacuum for M1.

Basically, reactants were pumped through the mixing volume, reactor, and back again. Three-way stopcocks S6 and S7 could be set to bypass the reactor. Traps T1 and T2 could be used to remove water during catalyst activation or to hold condensable reactants so that mixtures could be made. Total volume of the system was approximately 350 cc.

The reactor assembly could be removed intact by disconnecting it at J2 and J3. S8 could be closed to keep
FIGURE 5. Recirculation Reactor System
the catalyst from being exposed to air when the reactor assembly was removed. The catalyst was packed in the reactor between two glass wool plugs. A well protruding directly into the catalyst bed held a thermocouple that measured the catalyst temperature. A nichrome wire heater and temperature controller were used to maintain the reactor at any desired temperature.

The recirculation pump consisted of a glass cylinder and glass piston which was ground into the cylinder. The piston contained an iron core so that it could be oscillated back and forth via alternating magnetic fields which were provided by two solenoids surrounding the cylinder. The solenoids were alternately turned on by an electronic timer firing a Darlington type power transistor circuit. The frequency of oscillation was approximately one cycle per second and the pump displaced approximately 20 cc per cycle. Glass check valves V1-V4 were arranged as shown in Figure 5 to force flow in the clockwise direction.

**Flow Reactor System**

The flow reactor system shown in Figure 6 was used for kinetic measurements. The bulk of the system was constructed of Pyrex but valves V1-V4 were part of a metallic inlet system. Kovar to Pyrex seals were used for the transition from metal to glass. Tubing carrying helium to and from the chromatograph loop and capillary C3 were also made
FIGURE 6. Flow Reactor System
of metal. The tubing was fastened with epoxy cement onto the glass sidearms of stopcocks S7 and S8 to provide for low dead volume. The syringe pump was fabricated of aluminum and brass.

Hydrogen flow rate was determined by the setting of needle valve V3. The hydrogen flowed through capillary C2, and the pressure drop across C3 was measured by oil manometer M2. The pressure drop across the capillary provided a means for measuring the flow rate of hydrogen. The M2-C2 flow meter was calibrated with a soap bubble meter. The hydrogen flow could be stopped by closing stopcock S2.

Similarly, V2 controlled the flow rate of helium and the M1-C1 flow meter measured the flow rate. S1 could be used to shut off the helium flow. Any proportion of hydrogen to helium could thus be achieved.

The hydrogen or helium carrier gas travelled past the syringe pump where the reactant hydrocarbon was added. The section of glass immediately before and after the syringe pump input port was heated with nichrome wire to provide for rapid vaporization of the reactant hydrocarbon.

The syringe pump consisted of a synchronous motor driving a set of seven gears. Any one of the seven gears could be selected to drive an eighth gear, the master gear, which was set on a threaded shaft. A traveller moved in a channel down the threaded shaft as the master gear was driven. Any one of four gas-tight syringes were clamped
in front of the traveller and were emptied into the carrier gas as the traveller pushed the syringe plunger. Data for the syringe pump and syringes are given in Table 2.

A 250 cc mixing volume was included to help smooth any pulsations in the hydrocarbon concentration.

Three-way stopcocks S4 and S5 could be used to divert the flow either through or past the reactor. The reactor was identical to the type used in the recirculation system.

Three-way stopcocks S7 and S8, capillary C3, and trap T1 constituted the chromatograph sample loop. Samples were collected in T1 either by flow of products from the reactor through the trap or by expansion of a sample from a sample tube through S6 into previously evacuated T1. Helium carrier gas flowed through capillary C3 until S7 and S8 were rotated to allow the helium to flow through T1, sweeping out the sample. T1 was wound with nichrome wire to provide for sample heating if necessary.

Trap T2 was cooled in liquid nitrogen as necessary to remove radioactive samples from the reactor effluent.

EXPERIMENTAL PROCEDURES

Recirculation Experiments

Catalysts were activated by first evacuating the reactor and recirculation loop at ambient temperature. A flask fitted with a stopcock and ground glass joint and
<table>
<thead>
<tr>
<th>Gear #</th>
<th># of Teeth</th>
<th>.5 cc</th>
<th>1 cc</th>
<th>2.5 cc</th>
<th>5 cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>1.057</td>
<td>2.123</td>
<td>5.32</td>
<td>10.60</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>1.586</td>
<td>3.185</td>
<td>7.98</td>
<td>15.91</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>2.114</td>
<td>4.247</td>
<td>10.64</td>
<td>21.21</td>
</tr>
<tr>
<td>4</td>
<td>36</td>
<td>2.379</td>
<td>4.779</td>
<td>11.97</td>
<td>23.86</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>3.700</td>
<td>7.432</td>
<td>18.62</td>
<td>37.12</td>
</tr>
<tr>
<td>6</td>
<td>64</td>
<td>4.228</td>
<td>8.494</td>
<td>21.28</td>
<td>42.42</td>
</tr>
<tr>
<td>7</td>
<td>72</td>
<td>4.757</td>
<td>9.555</td>
<td>23.93</td>
<td>47.72</td>
</tr>
</tbody>
</table>

**PUMPING RATES**  µl/min

Motor speed - 1 rpm  
Master gear - 160 teeth  
Traveller screw - 20 threads per inch

*TABLE 2. Syringe Pump Data*
filled with hydrogen was inserted at J1. The neck of the flask was evacuated and a liquid nitrogen trap was placed at T2. The system was isolated from the vacuum by closing stopcocks S3 and S9; the reactor and recirculation loop were then filled to a pressure of 300 torr with hydrogen, which was measured with M1. The pump was turned on and the catalyst temperature was brought to 500°C. The activation continued for at least three hours. Water driven off the molecular sieve support was collected in T2.

After the activation was complete, the catalyst was cooled and the reactor bypassed via S6 and S7. Liquid nitrogen was removed from T2 and the trap was warmed. S5 and S9 were opened to evacuate the recirculation loop. Once the evacuation of the recirculation loop was complete, the reactor was evacuated. Care was taken never to evacuate the catalyst at high temperatures since this would have caused extensive tellurium loss. The catalyst did not require reactivation between reactions.

Hydrocarbon reactants were stored in individual sample tubes fitted with a stopcock and ground glass joint. The hydrocarbon was frozen in liquid nitrogen and the sample tube was evacuated. The stopcock was closed and the hydrocarbon was thawed. This freeze-pump-thaw outgassing procedure was repeated three times.

In preparation for a reaction, the reactor and recirculation loop were first evacuated and the reactor was
then bypassed. A sample tube containing the reactant hydrocarbon was connected at J1 and the neck of the tube was evacuated. The system was isolated from the vacuum by closing S3 and a desired pressure of the hydrocarbon was admitted to the system. If a second hydrocarbon was to be added, S5 was closed and the second sample tube inserted in J1. The neck of the sample tube and the tubing including S2-S5 were evacuated. Vacuum was closed off and S5 was opened. The second hydrocarbon was then added on top of the first hydrocarbon, and the difference in pressure was read on M1. All of the hydrocarbons were then condensed together in T2 with liquid nitrogen.

S5 was closed, a flask of deuterium or hydrogen was inserted at J1, and the neck evacuated. Vacuum was closed off and S5 was opened. Hydrogen or deuterium was added to the desired pressure. S5 was closed and the pump was turned on.

With the hydrocarbons still frozen in T2, S6 and S7 were rotated to admit the hydrogen or deuterium to the reactor. The catalyst temperature was then raised to reaction conditions. S6 and S7 were rotated to bypass the reactor and T2 was thawed to vaporize the hydrocarbons. The reactants were then mixed for at least 30 minutes. The reaction was started by rotating S6 and S7 to admit reactants to the reactor at time \( t = 0 \).
Samples were removed from the recirculation loop at any desired time. An empty sample tube was inserted at J1 and evacuated. S3 was closed and an aliquot of the reaction mixture was expanded through S5 into the sample tube. S5 was then closed.

If the samples were to be used for mass spectral analysis, the hydrocarbons in the sample tube were frozen in liquid nitrogen and the deuterium or hydrogen was evacuated. The sample tube was removed, thawed, and taken to the mass spectrometer for analysis.

Samples for gas chromatographic analysis were removed with the deuterium or hydrogen still in the mixture and taken to the sample loop on the Flow Reactor System. The tube was inserted in J3 on the flow system. S10 and S5 were closed, S9 and S6 were opened, and S7 and S8 were rotated so that the neck of the sample tube could be evacuated through T1. A liquid nitrogen trap was placed at T1 and the stopcock on the sample tube was opened slowly. Hydrogen and deuterium passed through T1 to vacuum but the hydrocarbons were frozen in T1. S7 and S8 were rotated to close off all parts, then T1 was heated. Switching S7 and S8 allowed the helium carrier gas to sweep the sample into the chromatograph. Samples eluting from the chromatograph could be frozen in liquid nitrogen for mass spectral analysis or collected in scintillation cocktail for radioactive analysis if desired.
Flow Reactor Experiments

Catalysts were activated on the flow reactor system by first adjusting a hydrogen flow rate of 30 cc per minute with V3. As hydrogen flowed through the catalyst bed, the reactor temperature was brought to 500°C. The activation continued for at least 12 hours. Once the activation was complete, the catalyst was cooled in hydrogen. Reactivation was not necessary between reactions.

Reactions were carried out by selecting a syringe and filling it with the desired hydrocarbon. Care was taken to eliminate any air bubbles. The syringe was inserted in the syringe pump and a hydrogen flow rate was selected. The catalyst was then brought to the desired reaction conditions. The master gear on the syringe pump was turned by hand until several drops of hydrocarbon dripped from the syringe needle into the hydrogen stream. The syringe pump was then set on the first gear. The hydrocarbon flow rate and the syringe pump pumping rate were left constant for one hour to let the hydrocarbon concentration stabilize.

After one hour, the effluent of the reactor was flowed through S7 and S8 to fill trap T1. S6 was opened to allow the reactor effluent flow to continue while S7 and S8 were switched to sweep the sample into the chromatograph.
While the chromatograph was analysing the first sample, the syringe pump was changed to a new pumping rate by changing gears. The hydrogen flow rate was changed proportionally to maintain the constant hydrocarbon concentration.

Once the first sample had completely eluted from the chromatograph, S8 and S7 were rotated to open T1, and S6 was closed to fill T1 with a new sample. This procedure was repeated until as many samples as desired were taken. A set of space velocities at constant inlet concentration of hydrocarbon was thus generated.

If a mixture of hydrogen and helium was desired, the same procedure was followed except both hydrogen and helium flow rates had to be changed in proportion to each other with the total change in flow rate being proportional to the change in hydrocarbon pumping rate.

**Toluene Dealkylation**

In radioactive tracer experiments using n-heptane $^1\text{H}^14\text{C}$, the toluene product had to be analysed for the ratio of side chain to aromatic ring radioactivity. A toluene dealkylation procedure, described below, was used to perform this task.

A 1 cc sample of toluene was refluxed for six hours in a solution of 5 g KMnO$_4$ in 30 cc of water. The mixture
was cooled and 5 g anhydrous Na₂SO₃ was added. The mixture was brought back up to refluxing conditions and 6 N H₂SO₄ was added dropwise until a clear solution was obtained. The mixture was cooled slowly to 0°C and the crystals were filtered off. The crystals were dissolved in a minimum amount of boiling water and recrystallized. The crystals were again removed by filtration and dissolved in 10 cc of 1 N NaOH. The solution was poured into a large test tube and warmed slightly. 1.7 g of AgNO₃ dissolved in 10 cc of warm water was then added dropwise. The mixture was centrifuged and the supernatant decanted. The precipitate was dried at 100°C. 20 cc of CCl₄ was added to slurry the precipitate and the mixture was heated to boiling. 20 cc of 0.5 N Br₂ in CCl₄ was added dropwise. The solution was then filtered and concentrated by boiling to a volume of 1 cc. Bromobenzene remaining in the solution was separated from the remaining CCl₄ by gas chromatography and analysed for radioactivity.
III - RESULTS

KINETIC MEASUREMENTS

Catalyst Aging

If a fresh catalyst was activated in flowing hydrogen for only 10 minutes at 500°C before beginning the reaction, the activity of the catalyst declined rapidly over the first hour. However, after about 5 hours, the activity of the catalyst became essentially constant.

Activating the catalyst for 12 hours in flowing hydrogen at 500°C resulted in a highly stable catalyst whose activity would drop only a few percent per week. The long activation periods appear to age the catalyst roughly the same as occurs during reaction. This indicates that tellurium loss, not carbon deposition, was responsible for the activity decline. Deposits of tellurium could be seen on the inside of the glass tubes located just downstream from the reactor. There was no evidence of carbon deposition on the catalyst except when the reactant was methylcyclopentane.
Therefore, all catalysts used for kinetic measurements were activated for at least 12 hours, and data which were directly compared were taken from runs over a span of not more than 3 days.

**Cyclohexane Kinetics**

To show that diffusion effects were not important in the cyclohexane reaction, three catalysts of different particle size were prepared. Activity measurements were conducted on the standard 40/60 mesh catalyst and also on catalysts with 20/30 mesh and 100/120 mesh particles. 250 mg of each catalyst were individually placed in a reactor and activated as usual. At a space velocity of $0.140 \text{ sec}^{-1}$, cyclohexane inlet concentration of $1.27 \times 10^{-3}$ moles/liter, and a reaction temperature of 520°C, the fractional conversions of cyclohexane over the 20/30 mesh, 40/60 mesh and 100/120 mesh particles were 0.552, 0.558, and 0.542, respectively. This result indicates that internal diffusion did not affect the reaction rates since the conversions were essentially the same.

In a second experiment, twice the amount of catalyst (500 mg of 40/60 particles) and twice the flow rate of reactants were used. The space velocity was therefore the same as in the previous experiment ($0.140 \text{ sec}^{-1}$) and the fractional conversion of cyclohexane at the same inlet
concentration and temperature was 0.547. This result shows that external diffusion effects are not important since the conversions were within experimental error of each other.

Figures 7, 8, and 9 are plots of space time versus conversion of cyclohexane for 540°C, 520°C, and 480°C respectively. Several inlet concentrations of cyclohexane were used at each temperature as indicated in the figures.

Benzene was by far the major product observed. Cracking products in all cases were less than one percent of the total hydrocarbons and were neglected for all calculations. Cyclohexene was the only other significant product observed. It appeared to be in equilibrium with the cyclohexane and constituted approximately two percent of the unreacted cyclohexane.

At first glance the reaction order appears to be slightly less than one since the inlet concentration of cyclohexane affects the conversion. However, dilution of cyclohexane due to production of hydrogen as the reaction proceeds can explain the results.

For a first order reaction:

\[ r_{\text{CH}} = k[\text{CH}] \]
FIGURE 7. Flow Reactor Experiment 1 with Cyclohexane
FIGURE 8. Flow Reactor Experiment 2 with Cyclohexane
FIGURE 9. Flow Reactor Experiment 3 with Cyclohexane
where:

\[ r_{CH} = \text{rate of disappearance of cyclohexane} \]
\[ k = \text{rate constant} \]
\[ [CH] = \text{concentration of cyclohexane} \]

The difficulty lies in finding a suitable expression for [CH] as a function of conversion. Neglecting the cyclohexene produced, the concentration of cyclohexane can be written:

\[ [CH] = \frac{M_{CH}}{F_{CH} + F_H + F_{BZ}} \]

where:

\[ M_{CH} = \text{molar flow rate of cyclohexane} \]
\[ F_{CH} = \text{volumetric flow rate of cyclohexane} \]
\[ F_H = \text{volumetric flow rate of hydrogen} \]
\[ F_{BZ} = \text{volumetric flow rate of benzene} \]

This expression can be written in terms of conversion as:

\[ [CH] = \frac{(M_{CH})_0 (1-x)}{(F_{CH})_0 (1-x) + x(F_{CH})_0 + 3x(F_{CH})_0 + (F_H)_0} \]  
\[ \text{(1)} \]

where:

\[ x = \text{fractional conversion of cyclohexane} \]
\[ (M_{CH})_0 = \text{initial molar flow rate of cyclohexane} \]
\[ (F_{CH})_0 = \text{initial volumetric flow rate of cyclohexane} \]
\[ (F_H)_0 = \text{initial volumetric flow rate of hydrogen} \]
The term \( x(F_{CH})_0 \) in the denominator represents the flow of benzene and the term \( 3x(F_{CH})_0 \) represents the 3 moles of hydrogen produced for each mole of cyclohexane reacted to form benzene.

Equation 1 can be put into a more usable form by rearrangement and substitution.

\[
[CH] = \frac{P(1-x)}{3x + R}
\]

where:

\[
P = \frac{(M_{CH})_0/F_{CH}}{(F_{CH})_0}
\]

\[
R = 1 + \frac{(F_H)_0/F_{CH}}{(F_{CH})_0}
\]

Thus:

\[
\dot{r}_{CH} = \frac{kP(1-x)}{3x + R} \tag{2}
\]

If we substitute equation 2 into the design equation for a plug-flow reactor, we obtain:

\[
\frac{V}{Q} = [CH]_0 \int \frac{dx}{kP(1-x)/(3x + R)}
\]

where:

\[
\frac{V}{Q} = \text{space time}
\]

\[
[CH]_0 = \text{inlet concentration of cyclohexane}
\]
Integration and evaluation of the constant of integration yields:

\[ k \frac{V}{Q} = \frac{[CH]_0}{p} \left[ -3x + (R + 3) \ln \left( \frac{1}{1-x} \right) \right] \] (3)

A plot of the right hand side of equation 3 versus V/Q should therefore give a straight line with slope k.

Table 3 summarizes the parameters for equation 3 calculated from data in Figures 7, 8, and 9. The ideal gas law was used as the equation of state when necessary. Figure 10 shows a plot of equation 3 for the data presented in Figures 7, 8, and 9.

Equation 3 evidently describes the data quite adequately. If k is calculated for each temperature from Figure 10, the values can be applied in an Arrhenius plot to determine the observed activation energy. Figure 11 shows such a plot which yields an activation energy of 40 Kcal/mole.

**Effect of Benzene**

From the data presented in Figure 7, it appears that product poisoning by benzene might also explain the apparent order being less than unity. To shed some light on the matter, an experiment was undertaken where radioactively labeled benzene was added to the cyclohexane reactant. Samples of cyclohexane and benzene were collected after
<table>
<thead>
<tr>
<th>TEMP. °C</th>
<th>SYMBOL</th>
<th>INLET CONCENTRATION moles/liter</th>
<th>R</th>
<th>P moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>Δ</td>
<td>1.24 x 10^{-3}</td>
<td>13.09</td>
<td>1.24 x 10^{-3}</td>
</tr>
<tr>
<td>520</td>
<td>○</td>
<td>2.03 x 10^{-4}</td>
<td>74.85</td>
<td>2.03 x 10^{-4}</td>
</tr>
<tr>
<td>480</td>
<td>●</td>
<td>1.97 x 10^{-3}</td>
<td>8.61</td>
<td>1.50 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td>□</td>
<td>5.20 x 10^{-3}</td>
<td>29.83</td>
<td>1.54 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td>■</td>
<td>1.27 x 10^{-3}</td>
<td>8.62</td>
<td>1.62 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td>△</td>
<td>2.02 x 10^{-3}</td>
<td>13.13</td>
<td>1.34 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>▸</td>
<td>5.33 x 10^{-4}</td>
<td>29.89</td>
<td>5.34 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>○</td>
<td>1.34 x 10^{-3}</td>
<td>13.09</td>
<td>5.61 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>□</td>
<td>2.84 x 10^{-4}</td>
<td>5804</td>
<td>2.13 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>●</td>
<td>5.61 x 10^{-4}</td>
<td>8.61</td>
<td>29.88</td>
</tr>
</tbody>
</table>

TABLE 3. Parameters and Symbols for Figure 10
FIGURE 10. Linearized Rate Equation Plot for Cyclohexane

See Table 3 for legend.
FIGURE 11: Activation Energy Plot for Cyclohexane
elution from the chromatograph and analysed for radioactivity. The cyclohexane, as expected, showed no radioactivity. The specific activity of the benzene product (when compared with the specific activity of the benzene entering the reactor) could be used to calculate the amount of benzene which was produced by the reaction of cyclohexane. The conversion of cyclohexane could therefore be determined.

Figure 12 shows the results of this experiment. In all runs, the inlet concentration of cyclohexane was constant at $2.7 \times 10^{-4}$ moles/liter. The results show that benzene does not affect the reaction rate and is therefore not a poison for the reaction.

**Effect of Hydrogen Concentration**

Another experiment was designed to determine the effect of hydrogen partial pressure on the reaction rate of cyclohexane.

First, assume the reaction scheme can be written:

\[
\begin{align*}
\text{CH} & \xrightleftharpoons[k_1']{k_1} \text{CH}^- + H_2 \\
\text{CH}^- & \xrightleftharpoons[k_2']{k_2} \text{CH}^{--} + H_2 \\
\text{CH}^{--} & \xrightleftharpoons[k_3']{k_3} \text{BZ} + H_2
\end{align*}
\]

Reaction Scheme II
FIGURE 12. Flow Reactor Experiment 4 with Cyclohexane
where:

\[ \text{CH} = \text{cyclohexane} \]
\[ \text{CH}^- = \text{cyclohexene} \]
\[ \text{CH}^{--} = \text{cyclohexadienes} \]
\[ \text{BZ} = \text{benzene} \]
\[ \text{H}_2 = \text{hydrogen} \]

If we make a steady state assumption for \( \text{CH}^- \) and \( \text{CH}^{--} \) and further assume elementary reactions, the reaction rate can be written as:

\[
\begin{align*}
\frac{\text{d}[\text{CH}]}{\text{dt}} &= \frac{k_1 k_2 k_3 [\text{CH}] - k_1' k_2' k_3' [\text{BZ}]}{k_1' k_2' [\text{H}_2]^2 + k_2' k_3' [\text{H}_2] + k_2 k_3} \\
&= \frac{k_1 k_2 k_3 [\text{CH}]}{k_1' k_2' [\text{H}_2]^2 + k_1' k_3' [\text{H}_2] + k_2 k_3}
\end{align*}
\]

The second term in the numerator of equation 4 represents the overall reverse rate of the reaction. The equilibrium constant at the temperatures of interest is such that below 10 atmospheres hydrogen pressure, the reverse reaction can be neglected, i.e. the reaction is for all practical purposes irreversible. Equation 4 then simplifies to:

\[
\begin{align*}
\frac{\text{d}[\text{CH}]}{\text{dt}} &= \frac{k_1 k_2 k_3 [\text{CH}]}{k_1' k_2' [\text{H}_2]^2 + k_1' k_3' [\text{H}_2] + k_2 k_3} \\
&= \frac{k_1 [\text{CH}]}{A_1 [\text{H}]^2 + A_2 [\text{H}] + 1}
\end{align*}
\]
where:

\[ A_1 = \frac{k_1'x_2'}{k_2x_3} \]
\[ A_2 = \frac{k_1'}{k_2} \]

The simplest way to evaluate the constants in equation 5 was to operate the flow reactor as a differential reactor. \( r_{CH} \) could be determined as a function of \([H_2]\) and the constants evaluated.

For a differential reactor:

\[ r_{CH} = [CH]_0 \frac{dx}{d(V/Q)} = \frac{x}{V/Q} [CH]_0 \]

and:

\[ [CH] = [CH]_0 (1 - x/2) \]

Figure 7 shows that the assumptions for a differential reactor should hold to conversions up to about 20 percent since the curve is reasonably linear in this range. Also, the expansion of reactants due to the production of hydrogen is negligible in this region.

Using equation 5 and rearranging gives:

\[ \frac{A_1[H_2]^2}{k_1} + \frac{A_2[H]}{k_1} + \frac{1}{k_1} = \frac{V/Q(1 - x/2)}{x} \]
Equation 6 is simply a quadratic equation in hydrogen concentration. The constants can be evaluated by plugging values of x for various values of \([H_2]\) into the equation.

Data were gathered by setting a hydrogen flow rate of 120 cc/minute and establishing a cyclohexane inlet concentration of \(1.24 \times 10^{-3}\) moles/liter. The conversion was measured at 540°C. Helium was then substituted for some of the hydrogen. The total flow rate and the inlet concentration of cyclohexane were held constant. Several helium to hydrogen ratios were used and the conversions were measured in each case. Conversions were less than 15 percent in all cases.

Figure 13 shows the results of the experiment. A quadratic least squares fit was used to generate the curve shown in Figure 13. The parameters calculated from the least squares fit are as follows:

\[
\begin{align*}
k_1 &= 5.03 \text{ sec}^{-1} \\
A_1 &= 1873 \text{ lt}^2 \text{mole}^{-2} \text{sec}^{-1} \\
A_2 &= 29.3 \text{ lt mole}^{-1} \text{sec}^{-1}
\end{align*}
\]

Figure 14 shows a slightly more usable form of the data. \(r_0\) in Figure 14 is the reaction rate in pure hydrogen.
FIGURE 13. Hydrogen Concentration Modelling for Cyclohexane Reaction
FIGURE 14. Effect of Hydrogen Concentration on the Reaction of Cyclohexane
**n-Hexane Kinetics**

Kinetics of the n-hexane reaction are more complicated than cyclohexane kinetics. The complication is due to the formation of significant quantities of n-hexenes as intermediates. Figure 15 shows the results of an n-hexane reaction at various inlet concentrations. The chromatogram indicated that the n-hexenes produced were in equilibrium with each other since several fused peaks were evident in the retention time region of the n-hexenes. Cracking products from the n-hexane reaction ranged from about 3 to 8 percent depending on the temperature. Cracking products were neglected for all calculations.

Since all the n-hexenes were in equilibrium with each other, they were considered as one species in the analysis. No other intermediates were detected. For kinetic purposes, let us assume the reaction proceeds as:

\[
\begin{align*}
H & \xrightarrow{k_1} H^* + H_2 \\
H^* & \xrightarrow{k_2} BZ + 3H_2
\end{align*}
\]

where:

- \(H\) = n-hexane
- \(H^*\) = n-hexenes
FIGURE 15. Flow Reactor Experiment 1 with n-Hexane
We can then express the rates of reaction as:

\[ -r_H = k_1[H] - k_1^*[H^*][H_2] \]  
(7)

\[ r_{H^*} = k_1[H] - k_1^*[H^*][H_2] - k_2[H^*] \]  
(8)

\[ r_{BZ} = k_2[H^*] \]  
(9)

where:

\[ r_i = \text{rate of appearance of species } i \]

Brackets indicate concentrations of the respective component.

Finding an analytical solution to equations 7, 8, and 9 is almost impossible. Equations 7 and 8 are coupled due to the reversibility of the hexane-hexene equilibrium. Furthermore, the concentrations of the respective components are not simple functions of conversion because of the production of hydrogen. The amount of hydrogen produced, and thus the extent of dilution of the reactants, is also a function of the selectivity of hexenes to benzene.

Equations 7, 8, and 9 were therefore solved numerically. The procedure used was to divide the flow reactor into a series of many differential reactors. The conversion was calculated assuming all the concentrations were constant over the first slice. A new flow rate was determined and concentrations corrected for the hydrogen produced and the resulting mixture was then used for the
calculations on the next slice. This process was repeated until enough slices had been accumulated to include the entire reactor. Initial estimates of $k_1$ and $k_2$ were made from the slopes of mole fraction versus space time curves shown in Figure 15.

Figure 16 shows the results of the numerical integration. Figure 17 and Figure 18 show similar calculations for reactions at 480°C and 540°C respectively. From the results, activation energy plots can be made for $k_1$ and $k_2$, as shown in Figures 19 and 20. Calculated apparent activation energies for $k_1$ and $k_2$ are 23 kcal/mole and 41 kcal/mole respectively. Due to the method employed for solving the rate equations, the apparent activation energies are probably not very accurate but are probably within 3 kcal/mole of the actual values.

OTHER REACTIONS

**n-Heptane Reaction**

Figure 21 shows a plot of the space time versus mole fraction of $C_6^+$ hydrocarbons for the reaction of n-heptane. The rate of the n-heptane reaction is significantly faster than the n-hexane reaction. The benzene produced is evidently a primary product, that is, it is not produced from the cracking of the toluene product. The selectivity of heptane to toluene at high conversions is approximately 90 percent.
FIGURE 16. Flow Reactor Modelling for n-Hexane Reaction
FIGURE 17. Flow Reactor Experiment 2 with n-Hexane
FIGURE 19. Activation Energy Plot for n-hexane Reaction
FIGURE 20. Activation Energy Plot 2 for n-Hexane Reaction
FIGURE 21. Flow Reactor Experiment with n-Heptane
C₈ Hydrocarbon Reactions

Table 4 summarizes the aromatic product distributions for n-octane and some of the dimethylcyclohexanes (DMCH's). Note that in every case, the most abundant products are those that can be obtained without rearrangement of the carbon skeletal structure.

Branched C₈ Reactions

Methylcyclopentane was also tested as a reactant in the flow reactor. No significant products were observed, but the catalyst was heavily coked during the reaction. Coking was never evident in any of the other reactions. The coking was probably due to dehydrogenation of the methylcyclopentane to methylcyclopentadiene which polymerized rapidly on the catalyst to produce coke.

2-Methylpentane gave no reaction products (except for a small percentage of cracking products) when passed over the catalyst at 520°C.

DEUTERIUM TRACER EXPERIMENTS

Cyclohexane with Deuterium

Figure 22 shows the conversion of cyclohexane as a function of time for a recirculation experiment with cyclohexane and deuterium. Samples were analysed on the mass spectrometer for the relative amounts of cyclohexane and
### Percentage of Aromatic Products

**Reactant**

<table>
<thead>
<tr>
<th>Products</th>
<th>n-octane</th>
<th>cis 1,3-DMCH</th>
<th>trans 1,3-DMCH</th>
<th>1,1-DMCH</th>
<th>cis 1,2-DMCH</th>
<th>cis 1,4-DMCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td>28.7</td>
<td>8.8</td>
<td>10.0</td>
<td>62.5</td>
<td>17.4</td>
<td>13.2</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>41.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>21.8</td>
<td>0</td>
<td>0</td>
<td>28.1</td>
<td>82.6</td>
<td>0</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>3.8</td>
<td>91.2</td>
<td>90.0</td>
<td>9.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>86.8</td>
</tr>
<tr>
<td>% Conversion</td>
<td>65.3</td>
<td>88.5</td>
<td>87.4</td>
<td>52.3</td>
<td>82.4</td>
<td>85.1</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>460</td>
<td>520</td>
<td>520</td>
<td>520</td>
<td>520</td>
<td>520</td>
</tr>
<tr>
<td>Contact Time (sec)</td>
<td>1.4</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

DMCH = dimethylcyclohexane

**TABLE 4.** Product Distributions from Various Reactants
FIGURE 22. Conversion Plot for Recirculation Experiment 1
benzene and simultaneously for the deuterium content of each species. Figure 23 shows the deuterium content of cyclclohexane and benzene as a function of time. In all calculations concerning isotopic species, corrections were first made for $^{13}\text{C}$ impurities by subtracting them from the spectra. $\phi$ is defined as:

$$\phi = \frac{\sum_{i=0}^{n} id_i}{\sum_{i=0}^{n} d_i}$$

where:

- $n$ = number of hydrogen atoms in the molecule
- $i$ = index
- $d_i$ = fraction of the molecules of a particular species containing $i$ deuterium atoms.

$\phi$ represents the average number of deuterium atoms contained in each molecule. In all cases, a statistical distribution of deuterium was present in the molecules, i.e., the distribution of deuterium was given by the binomial distribution function $f$ where $f$ is given by:

$$f(x,n,\theta) = \binom{n}{x} \theta^x (1-\theta)^{n-x}, \quad x = 0,1,2,...,n$$

$f$ is the probability of exactly $x$ successes in $n$ independent binomial trials with probability of success on a single trial equal to $\theta$. 
FIGURE 23. Deuterium Incorporation for Recirculation Experiment 1

- Benzene
- Cyclohexane

50 torr Cyclohexane
200 torr Deuterium

TIME (min.)

0 20 40 60 80 100 120 140 180 200 220

100 mg cat.

500°C
Cyclohexene with Deuterium

Figure 24 shows the hydrocarbon distribution for the cyclohexene reaction in the recirculation reactor as a function of time. The dehydrogenation of cyclohexene to benzene as well as the hydrogenation of cyclohexene to cyclohexane occurred simultaneously. The hydrocarbons were separated and analysed on the chromatograph, then each sample eluting from the chromatograph was collected and analysed for deuterium content on the mass spectrometer.

The results of the mass spectrometer analysis are shown in Figure 25. The percentage of deuterium in each species is plotted as a function of time. Percentage exchange is defined as $(\delta/n) \times 100$, where $n$ is the number of hydrogen atoms in the molecule. Note that the deuterium content was quite low so that the accuracy of the data is not great. The reason for the low levels of deuterium is the low temperature of the reaction. The temperature had to be reduced considerably to decrease the rate of cyclohexene reaction below the point where mixing in the recirculation reactor could influence the results.

Two things in Figure 25 should be noted. First, reactant cyclohexene is capable of exchanging deuterium, and secondly, the cyclohexane product has very little deuterium incorporation (approximately 1-2 percent exchange). If cyclohexane was formed by direct hydrogenation of cyclohexene with deuterium from the gas phase, the cyclohexane
FIGURE 24. Mole Fraction Plot for Recirculation Experiment 2
FIGURE 25. Deuterium Incorporation for Recirculation Experiment 2
would contain at least two deuterium atoms per molecule. Two deuterium atoms per molecule would result in a percentage exchange of 16.7. Even with the somewhat inaccurate data presented in Figure 25 (the values may be ± 25 percent), cyclohexane definitely does not contain 16.7 percent deuterium. We conclude that the formation of cyclohexane does not occur via direct gas phase hydrogenation of cyclohexene.

Figure 26 shows the selectivity of cyclohexane to benzene from the reaction shown in Figure 27. At zero conversion, the selectivity is approximately 40 percent.

From the deuterium exchange data, the following scheme can be used to explain the results:

1) \[ \text{CH} \xrightarrow{k_1} \text{CH}^- + \text{H}_2 \]

2) \[ 2\text{CH} \xrightarrow{k_2} \text{CH} + \text{CH}^- \]

3) \[ \text{CH}^- \xrightarrow{k_3} \text{CH}^- + \text{H}_2 \]

4) \[ \text{CH}^- \xrightarrow{k_4} \text{BZ} + \text{H}_2 \]

Reaction Scheme III
FIGURE 26. Selectivity Plot for Recirculation Experiment 2
Furthermore, deuterium incorporation must take place with olefins only.

Step two in the above sequence explains the low levels of deuterium incorporation in the cyclohexane product from the cyclohexene reaction. Step three is included to explain the selectivity of cyclohexane to benzene in the reaction of cyclohexene. Step four is probably very rapid since cyclohexadienes were never detected among the products. Two more experiments were performed to help shed light on the cyclohexane reaction scheme. These included the exchange of benzene with deuterium and the isomerization of methylcyclohexenes.

**Benzene Deuterium Exchange**

Figure 27 shows the results of a benzene-deuterium exchange reaction. A mixture of benzene-$d_0$, benzene-$d_6$, and deuterium was formulated in the recirculation reactor. During the course of the reaction, the benzene-$d_0$ did pick up some deuterium from the gas phase, but note that the rate was not very rapid (the ° scale is expanded). Benzene-$d_6$ did not pick up much hydrogen indicating that intermolecular exchange of hydrogen is not important.

**Methylcyclohexene Isomerization**

To show that the catalyst did indeed catalyze double bond migration, the methylcyclohexenes were isomerized. Figure 28 shows the product distribution from the reaction of 1-methylcyclohexene and Figure 29 shows
FIGURE 27. Recirculation Experiment 3

500 °C
100 mg col.

○ - D₀ BENZENE
□ - D₆ BENZENE

0.3
0.2
0.1
0.0
0.0

○
○
○
○

25 torr C₆H₆
25 torr C₆D₆
200 torr Deuterium

TIME (min.)
FIGURE 28. Recirculation Experiment 4
the product distribution from 3-methylcyclohexene. In both cases, 3- and 4-methylcyclohexene could not be separated on the gas chromatograph; thus the two compounds were analysed together and treated as a single species in all the calculations. The rate of isomerization was extremely rapid even at 370°C and was probably limited by mixing in the recirculation reactor.

RADIOACTIVE TRACER EXPERIMENTS

n-Hexane $\text{1}^{\text{14}}\text{C}$ Experiments

In order to establish that Step 1 in Reaction Scheme I (see page 6) is indeed the only possible first step in the reaction of n-hexane to form benzene, a series of radioactive tracer experiments with n-hexane $\text{1}^{\text{14}}\text{C}$ were undertaken.

Figure 30 shows the product distribution from a mixture of n-hexane $\text{1}^{\text{14}}\text{C}$ and cis-2-hexene reacted in the recirculation reactor. Figure 31 shows the results of the simultaneous collection and analysis of the radioactive content of each species. All the n-hexenes were collected together and rapid equilibration of the n-hexenes was evident. The first sample, collected after 30 minutes of reaction, showed essentially an equilibrium mixture of the n-hexenes.
FIGURE 31. Specific Activity Plot for Recirculation Experiment 6
Specific activities were calculated by taking the number of radioactivity counts per minute and dividing it by the normalized chromatographic area. \( \alpha_\infty \) is defined as the radioactive counts per minute of n-hexane divided by the sum of the chromatographic areas of n-hexane and \( cis-2 \)-hexene for the initial mixture. \( \alpha_\infty \) represents the specific activity that benzene would have if all the n-hexane and \( cis-2 \)-hexene were converted to benzene.

Several features of Figure 31 are important. First, the specific activity of the n-hexenes is always greater than the specific activity of benzene indicating that the n-hexane is at least converted more rapidly to n-hexenes than directly to benzene. Secondly, the n-hexane and the n-hexenes reach essentially the same specific activity indicating that hexane/hexene equilibrium is established. Also, the activities of all the species approach the required value of \( \alpha_\infty \) indicating that the data are internally consistent.

If benzene had come only from n-hexenes and not via direct ring closure of n-hexane, then the specific activity of the benzene product at zero conversion must be zero. Note that in Figure 31, there is some doubt about whether or not the benzene activity at zero conversion was zero because it was difficult to obtain reliable data at low conversions in this experiment. Therefore, a
second experiment at a lower temperature was performed so that low conversion data could be obtained.

The results of the low conversion run are shown in Figures 32 and 33. Figure 32 shows the product distribution and Figure 33 shows the results of the radioactive analysis. Note that the maximum percentage of benzene is less than 5 percent. Figure 33 shows fairly conclusively that the benzene activity at zero conversion is zero and therefore the benzene must come only from the n-hexenes. No direct ring closure of n-hexane occurs.

**n-Heptane $^{14}$C Experiment**

The recirculation reactor was filled with 20 torr of n-heptane $^{14}$C and 300 torr of deuterium and the reaction was started at 460°C. After 4 hours, all the products were trapped and removed from the reactor. All the reaction products were separated on the chromatograph but only the toluene product was collected. The overall conversion of the n-heptane $^{14}$C was about 85 percent. The toluene product was diluted to 1.1 cc with pure toluene. Several 2 μl samples of the diluted toluene were analysed for radioactivity; then 1 cc was used for toluene dealkylation. The bromobenzene product from the dealkylation was analysed for radioactivity and the specific activity of the toluene was compared to the specific activity of the bromobenzene. The bromobenzene showed
FIGURE 32. Mole Fraction Plot for Recirculation Experiment 7

50 torr n-Hexane $1^{-14}C$
8 torr cis-2-Hexene
400 torr Deuterium

440°C
200 mg. cat.
FIGURE 33. Specific Activity Plot for Recirculation Experiment 7
51.4 percent of the radioactivity of the toluene.

Toluene, in the simplest case, can be formed from n-heptane by only two routes. 1-6 carbon-carbon ring closure of the n-heptane $1^{-14}C$ or intermediates of n-heptane $1^{-14}C$ would yield toluene with the $14C$ tag in the 2 position of the aromatic ring. 2-7 carbon-carbon ring closure could result in the $14C$ tag being located in the toluene side chain. Other possibilities exist only if carbon skeletal rearrangement is possible. Since 51.4 percent of the radioactivity was found in the aromatic ring of the toluene, we conclude that essentially no carbon skeletal rearrangement took place in the reaction.

PHYSICAL MEASUREMENTS

Hydrogen Adsorption

Figure 34 shows the results of a hydrogen chemisorption isobar at 1 atmosphere pressure. The isobar was carried out on a standard volumetric type Pyrex apparatus with a mercury monometer.

The isobar was taken statically. The catalyst was evacuated at 200°C for 2 hours to remove water; then it was cooled to room temperature. A known quantity of hydrogen was added to the system. The volume of the system, including the catalyst sample, was adjusted to bring the pressure to 1 atmosphere. After 15 minutes, the amount of hydrogen adsorbed was measured and the catalyst temperature
FIGURE 34. Hydrogen Isobar
was raised to 100°C. The volume of the system was readjusted to keep the pressure constant and after 15 minutes the amount of hydrogen adsorbed was again measured. This process was repeated in 100°C intervals up to 500°C. Corrections were made for the expansion of hydrogen due to the increased temperature in the sample tube.

During the course of the isobar, tellurium was seen plated out on the walls of the sample tube just outside the heated zone of the tube. If we assume the catalyst contained 3 percent tellurium (after the loss of tellurium), the catalyst adsorbed 2 hydrogen atoms per tellurium atom at the maximum of the isobar. Note that the maximum amount of hydrogen adsorbed occurred near the melting point of tellurium which is 452°C.

ESC A

Table 5 summarizes the results of the ESCA studies. Two spectra were taken. The first spectrum was run on a sample of the NaX support alone and the second spectrum was run on an activated tellurium loaded NaX zeolite. There was a slight possibility of oxygen contamination of the catalyst during the transfer into the instrument through the nitrogen glovebox or in the instrument itself where the vacuum was not of the highest quality. Note that during the analysis, autoreduction of the Te$^{4+}$ took
<table>
<thead>
<tr>
<th></th>
<th>NaX Alone</th>
<th>Te/NaX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding* Energy(ev)</td>
<td>Relative # of Atoms</td>
</tr>
<tr>
<td>Te(3d)</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Na(1s)</td>
<td>1072.55</td>
<td>29.4</td>
</tr>
<tr>
<td>Al(2s)</td>
<td>119.15</td>
<td>17.3</td>
</tr>
<tr>
<td>Si(2p)</td>
<td>102.3</td>
<td>23.4</td>
</tr>
<tr>
<td>O (1s)</td>
<td>531.4</td>
<td>94</td>
</tr>
<tr>
<td>Na((\alpha))</td>
<td>574.0</td>
<td></td>
</tr>
<tr>
<td>O ((\alpha))</td>
<td>552.8</td>
<td></td>
</tr>
</tbody>
</table>

* Binding Energies corrected to C(1s) = 284.6 ev

** Te\(^+4\)(3d) dropped to zero after 30 min. of radiation

**TABLE 5. ES CA RESULTS**
place. This phenomenon is unusual but not unknown in ESC analysis in general. No increase in the TeO line was noted, however. Probably, TeO was being lost slowly into the vacuum due to its vapor pressure.

The important thing to notice about the two spectra is the shift in the sodium lines due to the addition of tellurium to the support. The Na(1s) line shifted 0.15 ev and the Na(α) line shifted 0.2 ev when the tellurium was added to the sieves. Although these shifts are not great, they are thought to be significant (26). This indicates that the tellurium is coordinated in some manner to the sodium in the support.

Sodium NMR

The results of three sodium NMR spectra are shown in Figure 35. The three samples were tellurium on NaX zeolite activated in hydrogen (Te/NaX/H₂), tellurium on NaX zeolite activated in deuterium (Te/NaX/D₂), and the NaX zeolite support alone.

The spectrum of the NaX support is quite different from the other two spectra. The main line is much broader and shifted very significantly to the left with respect to the other spectra. This indicates that the tellurium indeed has an effect on the sodium in the NaX sieves.
Scan range - 500 gauss
Time constant - 3 seconds
Receiver gain - 200
Field set - 17845 gauss
Scan time - 4 minutes
Microwave frequency - 20000 Hertz

FIGURE 35. NMR Results
Note that in the Te/NaX/H₂ and Te/NaX/D₂ spectra, there is a small band on the left shoulder of the main band. This shoulder is in roughly the same location as the main band in the spectrum of NaX alone and is probably due to sodium atoms in the NaX support that have not been affected by the addition of tellurium. Note also that the spectrum of the Te/NaX/H₂ is very similar to the Te/NaX/D₂ spectrum. The major difference is that the Te/NaX/H₂ spectrum is more complicated than the Te/NaX/D₂ spectrum. The difference is probably due to the spin-spin splitting of the sodium lines by the hydrogen. We therefore conclude that hydrogen is an integral part of any tellurium-sodium complex that exists in the catalyst. In my opinion, a thorough NMR study of sodium, tellurium, and hydrogen by an expert could yield complete information about the nature of the proposed tellurium-sodium-hydrogen complex in this catalyst.
IV - DISCUSSION

KINETICS AND REACTION SCHEMES

Cyclohexane Reaction

Two reaction schemes have been proposed for the reaction of cyclohexane. Reaction Scheme II (see page 57) and Reaction Scheme III (see page 82) differ only by the inclusion of Step 2 in Reaction Scheme III. However, it can be shown that Step 2 in Reaction Scheme III is important only when the concentration of cyclohexene is high. Assuming Step 2 is a second order reaction in cyclohexene and using the initial slope of the cyclohexene curve from Figure 24, \( k_2 \) in Reaction Scheme III can be calculated to be 424 liters/mole-sec per gram of catalyst at 440°C. If we assume an activation energy of 40 kcal/mole (this value is a good upper limit since the reaction is not very endothermic), at 540°C \( k_2 \) is \( 1.37 \times 10^4 \) moles/liter-second per gram of catalyst. When cyclohexane is used as the reactant, approximately 2 percent of the unreacted cyclohexane represents the amount of cyclohexene present. From the data in Figure 10, the rate of Step 1 in Reaction Scheme III is \( 3.28 \times 10^{-2} \) moles/liter-second at 540°C per gram of
catalyst at an inlet concentration of cyclohexane of $1.24 \times 10^{-3}$ moles/liter. The rate of Step 2, using the extrapolated value of $k_2$ and a cyclohexene concentration of $2.5 \times 10^{-5}$ moles/liter, is $8.40 \times 10^{-6}$ moles/liter-second per gram of catalyst. Thus, the rate of Step 2 is over 3 orders of magnitude slower than Step 1 and is negligible. Reaction Scheme II also gives the correct hydrogen concentration dependence on the reaction of cyclohexane.

The deuterium exchange data presented in Figure 23 can be explained by an olefin isomerization scheme. An olefin intermediate (either cyclohexene or cyclohexadiene) probably loses an allylic hydrogen to the surface followed by migration of the double bond. The olefin, now deficient one hydrogen in the original vinylic position, picks up a deuterium from the surface forming a deuterated species. Thus, the benzene product contains deuterium since olefin intermediates are involved in its production while cyclo-hexane cannot pick up deuterium because it is not olefinic.

The 40 Kcal/mole apparent activation energy reported for the cyclohexane reaction appears to be quite high for a catalytic reaction. However, considering the reaction is highly endothermic, 40 Kcal/mole is not unusual. The endothermicity of the cyclohexane reaction to benzene at 800°K is 53 kcal/mole (see Table 1).
The turnover frequency for the reaction of cyclohexane to benzene is 0.036 molecules of cyclohexane reacted per second per tellurium atom at 540°C, a cyclohexane concentration of $1.24 \times 10^{-3}$ moles/liter, and a hydrogen pressure of one atmosphere.

**n-Hexane Reaction**

Radioactive tracer experiments have shown that Step 1 in Reaction Scheme I (see page 6) proposed by Kazansky et al. (7) for chromia catalyst is also valid for the first step in this reaction over tellurium loaded zeolites. Silvestri and Smith (6) have shown that this scheme gives the correct reaction rate dependence on the hydrogen partial pressure. It appears that Reaction Scheme I is indeed the true scheme for this reaction over tellurium loaded zeolites.

The reported values of 23 and 41 Kcal/mole for the reaction of n-hexane to n-hexenes and n-hexenes to benzene, respectively, are not in good agreement with values reported by Panchenkov et al. (9) over chromia on alumina catalysts. However, Panchenkov et al. (9) reported that the reaction of n-hexane to form n-hexenes was the rate limiting step in the reaction of n-hexane to benzene, and this is in agreement with the data presented in this study. The activation energies reported in this work are not
unreasonable since the overall endothermicity of the reaction is about 64 Kcal/mole.

Silvestri and Smith (6) reported isohexanes as $C_6$ side products in the reaction of n-hexane to benzene over tellurium loaded zeolites. However, no isomerized hexanes were detected in experiments presented in this work and it appears that Silvestri and Smith (6) may have mistakenly identified the n-hexene peaks in their chromatographic results as isohexanes.

**n-Heptane Reaction**

It seems reasonable to assume that toluene is formed from n-heptane via a similar scheme by which benzene is formed from n-hexane. Consecutive dehydrogenation of n-heptane to 1,3,5-heptatriene followed by thermal cyclization to methycyclohexadiene would indeed yield toluene. A scheme of this sort would also explain the radioactive tracer result that 51.4 percent (essentially half) of the radioactivity was found in the aromatic ring after the reaction of n-heptane $1^{-14}C$ to toluene.

There remain at least two pieces of seemingly contradictory information. First, chromia catalysts should give the same results as the tellurium loaded zeolites since they appear to promote similar reaction schemes. However, the radioactive tracer studies of Mitchell (11)
and Chen et al. (12) showed that chromia catalysts do not necessarily give half the radioactivity in the toluene side chain from the reaction of n-heptane \(^{1-14}\text{C}\), as tellurium loaded zeolites do. Secondly, benzene was found as a primary product in the reaction of n-heptane over tellurium loaded zeolite. It is possible to resolve both these unanswered questions with the following arguments.

1,3,6-heptatriene is certainly a possible product from the consecutive dehydrogenation of n-heptane, though 1,3,5-heptatriene should be much more thermodynamically favorable due to the conjugation of the double bonds. If a small amount of 1,3,6-heptatriene is produced, thermal cyclization would probably yield cycloheptadiene. The fate of this cycloheptadiene is uncertain. I would suggest that over tellurium loaded zeolites, a \(C_7\) to \(C_6\) ring collapse occurs which simultaneously splits out one carbon. The \(C_6\) ring eventually yields benzene and the carbon split off winds up as methane. This would explain the result that benzene is a primary product in the reaction of n-heptane over tellurium loaded zeolites. The proportion of toluene to benzene (roughly 9 to 1) also seems to be a reasonable value for the ratio of 1,3,5-heptatriene to 1,3,6-heptatriene, since thermodynamics favors 1,3,5-heptatriene.
I would further suggest that the fate of the proposed cycloheptatriene over chromia catalysts involves statistical C\textsubscript{7} to C\textsubscript{6} ring collapse (without splitting out methane) eventually yielding toluene. Radioactive tracers would be found anywhere in the compound after this procedure and the amount of radioactivity in the toluene side chain would be less than 50 percent as found by Mitchell (11) and Chen \textit{et al.} (12). But Chen \textit{et al.} (12) found 17.4 percent radioactivity in the toluene side chain from the reaction of n-heptane 1\textsuperscript{14}C over pure chromia, and the proposed scheme could not explain side chain radioactivity levels that low. Perhaps the chromia catalyst rearranges the heptane skeletal structure to say 2- or 3-methylhexane prior to cyclization. A scheme of this type could explain the radioactive levels found in the toluene side chain by Chen \textit{et al.} (12).

**Branched C\textsubscript{6} Reactions**

The results of the reactions of methylcyclopentane and 2-methylpentane basically show that the tellurium loaded zeolite has no activity for carbon skeletal rearrangement since no aromatic products were observed. Like chromia, the catalyst's unfortunate ability to polymerize methylcyclopentane decreases its attractiveness for industrial reforming applications.
C₃ Hydrocarbon Reactions

Armed with the knowledge discussed to this point, one can predict with considerable reliability the reaction products that are presented in Table 4. The major aromatic products obtained from each reaction are those expected if no skeletal rearrangement takes place. A few points, however, warrant discussion.

n-Octane can form ethylbenzene by two routes. 1-6 ring closure or 3-8 ring closure of an octatriene would yield ethylbenzene. o-xylene can be formed in only one way: by 2-7 ring closures of 2,4,6-octatriene. Thus, one would expect 2 moles of ethylbenzene for every mole of o-xylene in the products if no steric hindrances or thermodynamic restrictions apply. To a good approximation, the results bear out this prediction since the ethylbenzene/o-xylene ratio is 1.88.

The formation of benzene and toluene from n-octane probably occurs via a methyl or ethyl loss similar to the way benzene is formed from the reaction of n-heptane.

Note also that all the dimethylcyclohexanes (DMCH's) except 1,1-DMCH gave about the same conversions under the same reaction conditions. Also, the only products detected were toluene and the xylene corresponding to the same skeletal structure as the DMCH. 1,1-DMCH did not react as rapidly as the other DMCH's since it cannot form an
aromatic product without demethylation or skeletal rearrangement. The major reaction product from 1,1-DMCH is toluene produced by demethylation. If the methyl group that is removed from the 1 position in 1,1-DMCH becomes attached to another ring carbon, we would expect o-xylene to be the most likely product followed by m-xylene and then p-xylene because of the proximity of the methyl group to the corresponding ring positions. The results show that this is the case. The aromatic distribution from the reaction of 1,1-DMCH is very similar to the distribution reported by Davis (15) over chromia catalysts.

THE NATURE OF THE ACTIVE SITE

Although evidence about the exact solid state nature of the active site is sparse, considerable speculation about the sites has been presented. We will review some of this material in the light of the new data that has been obtained. Several findings on the solid state nature of tellurium loaded zeolites reported by Mikovsky et al. (4) and Olson et al. (5) are not in agreement with findings in this work.

The most glaring difference is the ESCA results which show no Te$^{2-}$ ions on the surface while Mikovsky et al. (4) and Olson et al. (5) reported that Te$^{2-}$ is the active surface species. Furthermore, their model suggested that
tellurium reacts with hydrogen to form the Te\(^{2-}\) and leaves H\(^+\) ions on the surface. This reaction probably would not reverse as the temperature is increased, i.e., H\(^+\) ions would not remove electrons from the Te\(^{2-}\) ion and leave as hydrogen gas. However, Figure 34 shows that the uptake of hydrogen is indeed reversible, and this result suggests that a simple chemisorption of hydrogen is involved.

However, NMR results and ESCA results support the results of Mikovsky et al. (4) and Olson et al. (5) in the finding that the alkali metal associated with the zeolite forms some sort of coordination complex with tellurium. A perplexing result was discovered when a LiX zeolite was prepared in a similar manner as the KX zeolite prepared by Mikovsky et al. (4). Even though the LiX zeolite showed a high surface area (600 m\(^2\)/g), when loaded with tellurium, it was not an active catalyst. The model for the active site proposed by Mikovsky et al. (4) and Olson et al. (5) cannot explain this result.

The results of this study suggest that Te\(^0\) loosely coordinated to the p-electrons of the cation on the zeolite surface is the active species. Since lithium does not contain p-electrons, LiX zeolite would not be an active catalyst while NaX, KX, CeX, and RbX would. This is in agreement with the findings in both this study and the study by Mikovsky et al. (4). The tellurium-cation coordination is
probably not strong enough to overcome completely the vapor pressure of tellurium, and thus tellurium would be slowly eluted from the support. Chemisorption of hydrogen (probably two hydrogen atoms per tellurium atom) would yield a partial positive charge on each hydrogen and a partial negative charge on the tellurium atom. The partial negative charge on the tellurium atom would stabilize the tellurium-cation coordination. Therefore, a hydrogen atmosphere would maintain the tellurium on the support while a helium atmosphere would allow tellurium to be lost. A model of this type explains the tellurium elution by helium discovered by Mikovsky et al. (4). The simple chemisorption of hydrogen also explains the reversibility of hydrogen uptake presented in Figure 34.

The results of this study do not shed any immediate light on the position of the tellurium atom or the number of zeolite cations involved in the surface coordination. The NMR results probably contain much of the information but the complete interpretation of the NMR results is an impossibility without extensive study by some expert in the field. The suggestion of Mikovsky et al. (4) and Olson et al. (5) that tellurium atoms are associated with Site II and Site III cations in the zeolite supercage seems quite reasonable.
REACTION MECHANISMS

Assuming that Te\(^0\) loosely coordinated to the cations on the zeolite support is the active species, we can speculate on the surface reaction mechanisms.

The tellurium active site evidently has a strong affinity for hydrogen since it will adsorb 2 hydrogen atoms per tellurium atom. Tellurium atoms with only one hydrogen atom adsorbed are probably also present on the surface at reaction conditions since the catalyst does promote hydrogen-deuterium exchange. At reaction conditions, the tellurium sites are probably in rapid adsorption-desorption equilibrium with the hydrogen gas phase. The active site probably has little affinity for forming an adsorption with a carbon atom or the catalyst would probably promote skeletal isomerization or more extensive cracking reactions.

**Dehydrogenation Mechanism**

A simple dehydrogenation probably proceeds via:

\[
\begin{align*}
\text{H}_2\text{C} = \text{C} + \text{Te} & \rightarrow \text{H}_2\text{C} = \text{C} - \text{H} + \text{Te} \text{H} \quad 1; \\
\text{H} \quad \text{H} & \\
\text{H} \quad \text{Te} & \\
\text{Te} &
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} = \text{C} + \text{Te} & \rightarrow \text{Te} + \text{H}_2 \quad 2)
\end{align*}
\]
where:

\[ \text{Te} = \text{active tellurium site} \]

Step 1 must be irreversible or the cyclohexane formed during the reaction of cyclohexene (see Figure 25) would be highly deuterated. Data taken in our laboratory by another worker (27) showing that the reaction of cyclohexane is about twice as rapid as the reaction of perdeuterated-cyclohexane supports the requirement that two hydrogen atoms are removed simultaneously and that the removal of the hydrogens is the rate limiting step. A stepwise removal of hydrogen would probably require either a carbon-tellurium adsorption or deuterium incorporation into the paraffin. Figure 23 shows that cyclohexane does not undergo deuterium exchange.

**Olefin Deuterium Exchange Mechanism**

The mechanisms involving the incorporation of deuterium into olefins probably proceeds via an active site which is deficient of one hydrogen atom. The mechanism might involve:

\[
\begin{align*}
\text{D} & \quad \text{Te} + \\
\text{H} & \quad \text{C} = \text{C} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{C} \\
\text{D} & \quad \text{Te} \\
\end{align*}
\]
Once the complex in Step 1 has been formed, the complex cannot break down and leave the tellurium site with two hydrogen atoms or an allenic diene would be formed. The high instability of allenic dienes discounts this possibility. The breakdown of the complex can go either way, either yielding a deuterated olefin or reversing to the original non-deuterated olefin. Note that only an olefin could undergo a deuterium exchange via this mechanism because the molecule must be able to accept a hydrogen as well as lose one. Isomerization of olefins would be very rapid compared to dehydrogenation since only one C-H bond has to be broken. This is in agreement with the results found in this study.

**Cyclohexene Disproportionation Mechanism**

The disproportion of cyclohexene to form cyclohexane and cyclohexadiene reported in Reaction Scheme III (see page 82) is difficult to envisage. Adsorption of two cyclohexene molecules on adjacent sites followed by hydrogen exchange between the two molecules is unlikely
because most of the tellurium active sites are probably too far apart. Adsorption of two cyclohexene molecules on a single site is more likely. Letting \( R, R', \) and \( R'' \) represent cyclohexane, cyclohexene, and cyclohexadiene rings, respectively, the mechanism might be:

\[
2 \ R'^{-}H \ + \ Te \ \rightarrow \ R' \quad \text{1)}
\]

\[
\begin{array}{c}
R' \\
H \\
Te
\end{array} + \begin{array}{c}
R' \\
H \\
Te
\end{array} \rightarrow \begin{array}{c}
R'' \\
H \\
Te
\end{array} + \begin{array}{c}
R' \\
H \\
Te
\end{array} \quad \text{2)}
\]

\[
\begin{array}{c}
R \\
H \\
Te
\end{array} + \begin{array}{c}
R' \\
H \\
Te
\end{array} \rightarrow \begin{array}{c}
R'' \\
H \\
Te
\end{array} + \begin{array}{c}
R' \\
H \\
Te
\end{array} \quad \text{3)}
\]

The proximity of the cyclohexene molecules makes the exchange of hydrogen between the molecule possible, but the driving force for the exchange is not evident. Other olefins could probably undergo the same type of disproportionation.

Each of the mechanisms presented is consistent with the findings in this work. However, completely unambiguous evidence for most of these mechanisms still has not been reported. Mechanisms involving the cracking activity of the tellurium loaded zeolites have been
purposely overlooked because the cracking activity was not studied in this work. There is ample room for considerably more work to establish the fine details of this interesting and useful catalytic reaction.
V - SUMMARY

Dehydrocyclization reactions play an important role in the reforming of napthas to yield high octane gasolines. The discovery of tellurium loaded zeolite dehydrocyclization catalysts in 1970 coupled with the industrial importance of catalysts of this type induced this research work into the active nature of this catalyst.

Kinetic measurements on the reactions of cyclohexane and n-hexane over tellurium loaded zeolites to yield benzene have shown that in both cases the reaction is first order in the respective reactant. The apparent activation energy for the reaction of cyclohexane is 40 kcal/mole. The reaction of n-hexane to benzene proceeds, for kinetic purposes, through the n-hexenes as intermediates. The apparent activation energy for dehydrogenation of n-hexane to the n-hexenes is 23 kcal/mole; for the aromatization of n-hexenes it is 41 kcal/mole.

Deuterium exchange experiments with cyclohexane and cyclohexene have helped establish the following reaction scheme for the reactions of cyclohexane and cyclohexene:
cyclohexane  $\rightarrow$ cyclohexene + $\text{H}_2$  (1)

2 cyclohexene  $\rightarrow$ cyclohexane + cyclohexadiene  (2)

cyclohexene  $\rightarrow$ cyclohexadiene + $\text{H}_2$  (3)

cyclohexadiene  $\rightarrow$ benzene + $\text{H}_2$  (4)

However, mathematical models based on the observed kinetics indicate that Step 2 in the above sequence is negligible during the reaction of cyclohexane. Thus, the following reaction scheme, supported by hydrogen concentration rate dependence measurements, is the preferable reaction scheme for the reaction of cyclohexane:

cyclohexane  $\rightarrow$ cyclohexene + $\text{H}_2$  (1)

cyclohexene  $\rightarrow$ cyclohexadiene + $\text{H}_2$  (2)

cyclohexadiene  $\rightarrow$ benzene + $\text{H}_2$  (3)

Radioactive tracer experiments with n-hexane $1^{-14}\text{C}$ have shown that the n-hexane proceeds only through the n-hexenes on the route to form benzene over tellurium loaded zeolites. More radioactive tracer work could help establish other intermediates in the n-hexane reaction, but all the evidence in this work points to the following reaction scheme for the aromatization of n-hexane:

n-hexane  $\rightarrow$ n-hexenes + $\text{H}_2$

n-hexenes  $\rightarrow$ hexadienes + $\text{H}_2$

hexadienes  $\rightarrow$ hexatriene + $\text{H}_2$

hexatriene  $\rightarrow$ cyclohexadiene

cyclohexadiene  $\rightarrow$ benzene + $\text{H}_2$
Radioactive tracer experiments with n-heptane 1$^{14}$C, C$_8$ cyclic and non-cyclic paraffin reactions, and branched C$_6$ reactions have established that tellurium loaded zeolites have little activity for carbon skeletal rearrangement.

Sodium NMR and ESCA solid state studies show that tellurium is coordinated to the cations in the zeolite support. The lack of activity of tellurium loaded on LiX zeolites indicates that the tellurium coordination is with the p-electrons of the zeolite cations. Hydrogen adsorption measurements along with ESCA results indicate that the active surface species is an elemental tellurium atom which is capable of adsorbing two hydrogen atoms per tellurium atom. Tellurium NMR and tellurium Mössbauer work could yield significantly more information on the structure of the active site.

Reaction mechanisms, consistent with kinetic observations, isotopic tracer data, and solid state measurements have been proposed. A simple dehydrogenation probably consists of a single step during which two hydrogen atoms are simultaneously abstracted from a molecule by the tellurium active site.
REFERENCES


26) Wagner, C., private communication.

27) Ismagilov, Z., to be published.