RICE UNIVERSITY

THE CATALYTIC CRACKING OF CUMENE OVER SILICA-ALUMINA.
A STUDY WITH STABLE AND RADIOACTIVE TRACER COMPOUNDS.

by

ALEJANDRO J. AZUAJE-FERNANDEZ

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

MASTER OF ARTS

APPROVED, THESIS COMMITTEE:

Joe W. Hightower, Professor in the
Department of Chemical Engineering,
Chairman

Phillip R. Brooks, Professor of
Chemistry

Robert F. Curl, Professor of Chemistry

HOUSTON, TEXAS

JUNE, 1980
ABSTRACT

THE CATALYTIC CRACKING OF CUMENE OVER SILICA-ALUMINA.
A STUDY WITH STABLE AND RADIOACTIVE TRACER COMPOUNDS.

by

Alejandro Jose Azuaje-Fernandez

The catalytic cracking of cumene (iso-propyl benzene) over a silica-alumina catalyst (Houdry M-46) has been studied using the pulse technique in a microcatalytic reactor. The initial deactivation of the catalyst was found to follow an empirical first order equation with respect to the initial activity towards the formation of products. Cumene is given as the precursor of the coke formed at the surface of the catalyst. As in (18) the deactivation is thought to proceed by a Hinshelwood mechanism in which two sites are lost in every deactivating event or adsorption of the poison on two sites. The rate of the cracking reaction is described by a first order equation in reactant cumene and is proposed to follow a Langmuir-Hinshelwood mechanism in the range of 250°C to 400°C and 1.67 atm. The true activation energy of the reaction was found to be 21.4 kcal mole⁻¹. Experiments with H-D exchange over this catalyst showed that deuterium distribution in either benzene and cumene occurred to statistical scrambling at equilibrium, indicating the lability of the C-H bonds in the hydrocarbons. D-H exchange measurements gave as result \(1.8 \times 10^{18}\) sites/m² and is set as an upper limit for the active sites on the catalyst surface if Brønsted centers are thought to be the active centers for the dealkylation. Results of experiments with radioactive tracer compounds indicated that the reaction proceeded to almost equili-
illibrium without influence of the back reaction. Values, based on a reaction model of a first order reversible process occurring near equilibrium, obtained for thermodynamic functions for the cracking reaction are reported. These values are in good agreement with the theoretical values obtained from the standard functions of formation of the reaction participant compounds.
ACKNOWLEDGEMENTS

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

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

Professors P.R. Brooks and R.F. Curl for serving on the oral committee.

Consejo Nacional de Investigaciones Científicas y Tecnológicas CONICIT for providing financial support.

Universidad Simon Bolivar for financial support.

Welch Foundation Grant Number C-316.

National Science Foundation Grant Number CHE 77-10541.

My co-workers in the Laboratory of Catalysis in the Chemical Engineering Department at Rice University for providing helpful suggestions and encouragement as well as many good times.

Mr. and Mrs. Alejandro Azuaje Rincon, my parents, for their affection, love, and comprehension.

Mrs. Carolina Azuaje, my wife, for her love, encouragement and support.

Mrs. Pat Angel, for her time and dedication in typing this thesis.
TABLE OF CONTENTS

I. INTRODUCTION .................................................. 1
   Previous work on silica-alumina catalysts ............ 4
   Previous work in catalysts other than
   silica-alumina .............................................. 9
   Isotopic tracer studies ................................. 14
   Thermodynamics ............................................ 17
   Objectives .................................................. 17

II. EXPERIMENTAL ................................................. 20
   Catalyst ..................................................... 20
   Chemicals .................................................. 20
   Apparatus .................................................. 21
      Microcatalytic reactor and gas chromatograph ... 21
      Mass spectrometer .................................... 25
      Liquid scintillation counter ....................... 25
   Experimental procedures ............................... 26
      Determination of response factors ................. 26
      Kinetic experiments .................................. 28
      Constant temperature experiments ................. 28
      Variable temperature experiments ............... 29
      Deactivation experiments ......................... 30
      Isotopic tracer experiments ....................... 32
      Radioactive tracer experiments ................. 35

III. RESULTS ..................................................... 37
   Deactivation measurements ............................ 37
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic measurements</td>
<td>44</td>
</tr>
<tr>
<td>First order kinetics</td>
<td>44</td>
</tr>
<tr>
<td>Kinetic parameters for the first order approximation</td>
<td>46</td>
</tr>
<tr>
<td>Deuterium tracer experiments</td>
<td>54</td>
</tr>
<tr>
<td>Radioactive tracer experiments</td>
<td>79</td>
</tr>
<tr>
<td>IV. DISCUSSION</td>
<td>93</td>
</tr>
<tr>
<td>Deactivation of the catalyst and kinetics</td>
<td>93</td>
</tr>
<tr>
<td>Deuterium tracer results</td>
<td>99</td>
</tr>
<tr>
<td>Nature of the active sites</td>
<td>101</td>
</tr>
<tr>
<td>Reversibility of the dealkylation reaction</td>
<td>104</td>
</tr>
<tr>
<td>Reaction mechanism</td>
<td>105</td>
</tr>
<tr>
<td>V. SUMMARY</td>
<td>107</td>
</tr>
<tr>
<td>VI. REFERENCES</td>
<td>109</td>
</tr>
<tr>
<td>APPENDIX I</td>
<td>112</td>
</tr>
<tr>
<td>APPENDIX II</td>
<td>117</td>
</tr>
<tr>
<td>APPENDIX III</td>
<td>122</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Thermodynamic functions for the dealkylation of iso-propyl benzene</td>
<td>18</td>
</tr>
<tr>
<td>II</td>
<td>Equilibrium conversion for the dealkylation of iso-propyl benzene</td>
<td>18</td>
</tr>
<tr>
<td>III</td>
<td>Isotopic composition of products in microcatalytic tracer experiments</td>
<td>63</td>
</tr>
<tr>
<td>IV</td>
<td>Isotopic tracer results. Injection of $\text{C}_6\text{D}_6$. $T = 578 \text{ K}$</td>
<td>64</td>
</tr>
<tr>
<td>V</td>
<td>Isotopic tracer results. Injection of $\text{C}_6\text{D}_6$. $T = 598 \text{ K}$</td>
<td>64</td>
</tr>
<tr>
<td>VI</td>
<td>Isotopic tracer results. Injection of $\text{C}_6\text{D}_6$. $T = 628 \text{ K}$</td>
<td>65</td>
</tr>
<tr>
<td>VII</td>
<td>Isotopic tracer results. Injection of $\text{C}_6\text{D}_6$. $T = 653 \text{ K}$</td>
<td>65</td>
</tr>
<tr>
<td>VIII</td>
<td>Isotopic tracer results. Injection of $\text{C}<em>9\text{H}</em>{12}$. $T = 578 \text{ K}$</td>
<td>66</td>
</tr>
<tr>
<td>IX</td>
<td>Isotopic tracer results. Injection of $\text{C}<em>9\text{H}</em>{12}$. $T = 598 \text{ K}$</td>
<td>66</td>
</tr>
<tr>
<td>X</td>
<td>Isotopic tracer results. Injection of $\text{C}<em>9\text{H}</em>{12}$. $T = 628 \text{ K}$</td>
<td>67</td>
</tr>
<tr>
<td>XI</td>
<td>Isotopic tracer results. Injection of $\text{C}<em>9\text{H}</em>{12}$. $T = 653 \text{ K}$</td>
<td>67</td>
</tr>
<tr>
<td>XII</td>
<td>Thermodynamic properties for the equilibrium reaction $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_7 \rightleftharpoons \text{C}_6\text{H}_6 + \text{C}_3\text{H}_6$</td>
<td>91</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Instrumental Assembly</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Chromatogram of Prouducts of Reaction</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>Schematic for collection of compounds for Mass Spectroscopic analysis</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>Chromatogram indicating switching of valve V5 for collection of cumene</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Decay of activity with pulse number</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>First Order decay plot</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>Effect of inhibitors on catalyst activity</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>Effect of inhibitors on catalyst activity during long runs</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>Relationship of % conv, number of moles recovered, and number of moles lost</td>
<td>43</td>
</tr>
<tr>
<td>10</td>
<td>Test for first order kinetics</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>Arrhenius plot. Benzene and propylene as products</td>
<td>48</td>
</tr>
<tr>
<td>12</td>
<td>Arrhenius plot. Benzene, propylene and ethyl benzene as products</td>
<td>49</td>
</tr>
<tr>
<td>13</td>
<td>Product distribution with Temperature</td>
<td>51</td>
</tr>
<tr>
<td>14</td>
<td>Deuterium distribution in benzene, d_i versus 1/PN. Comparison with binomial</td>
<td>57</td>
</tr>
<tr>
<td>15</td>
<td>Deuterium distribution in benzene. PN1 and PN2</td>
<td>58</td>
</tr>
<tr>
<td>16</td>
<td>Deuterium distribution in benzene. PN3 and PN4</td>
<td>59</td>
</tr>
<tr>
<td>17</td>
<td>Deuterium distribution in benzene. PN5 and PN6</td>
<td>60</td>
</tr>
<tr>
<td>18</td>
<td>Average number of atoms exchanged per molecule as function of pulse number.</td>
<td>68</td>
</tr>
<tr>
<td>19</td>
<td>Cumulative number of atoms exchanged versus the pulse number.</td>
<td>68</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>20</td>
<td>Average number of atoms exchanged per molecule as function of pulse number.</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>$T = 598 , K$</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Cumulative number of atoms exchanged versus the pulse number.</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>$T = 598 , K$</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Average number of atoms exchanged per molecule as function of pulse number.</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>$T = 628 , K$</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Cumulative number of atoms exchanged versus the pulse number.</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>$T = 628 , K$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Average number of atoms exchanged per molecule as function of pulse number.</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>$T = 653 , K$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Cumulative number of atoms exchanged versus the pulse number.</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>$T = 653 , K$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Reciprocal of the cumulative number of atoms exchanged versus $1/\text{PN}$</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>for the passage of $\text{C}_6\text{D}_6$</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Reciprocal of the cumulative number of atoms exchanged versus $1/\text{PN}$</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>for the passage of $\text{C}<em>8\text{H}</em>{12}$</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Mass spectras of a) cumene blank and b) cumene PN7</td>
<td>76</td>
</tr>
<tr>
<td>29</td>
<td>Mass spectras of a) cumene PN8 and b) cumene PN9</td>
<td>78</td>
</tr>
<tr>
<td>30</td>
<td>Deuterium distribution in cumene. PN7 and PN8,</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>$T = 598 , K$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Deuterium distribution in benzene. PN7 and PN8,</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$T = 598 , K$</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Activity of benzene and cumene after passage of a mixture cumene:benzene-$^{14}\text{C}$ over catalyst. a) $325,\text{°C}$ and</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>b) $350,\text{°C}$</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Activity of benzene and cumene after passage of a mixture cumene:benzene-$^{14}\text{C}$ over catalyst. a) $375,\text{°C}$ and</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>b) $400,\text{°C}$</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>$%$ conv as a function of contact time. a) $325,\text{°C}$ and</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>b) $350,\text{°C}$</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>$%$ conv as a function of contact time. a) $375,\text{°C}$ and</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>b) $400,\text{°C}$</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Reciprocal of $X$ versus $1/\tau$</td>
<td>88</td>
</tr>
<tr>
<td>37</td>
<td>Plot for the determination of $\Delta H^O$</td>
<td>90</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

The cracking of petroleum fractions is the process in which high molecular weight hydrocarbons are converted into material with a lower molecular weight (1,2). The process was initially introduced in the U.S.A. in 1912 and was carried out thermally. The initial objective was simply to increase the amount of gasoline from crude oil. However, as the compression ratio of the automobile engines increased, it was discovered that the gasoline produced by cracking possessed a higher octane rating and burned more smoothly in the engines than did the "straight run" gasoline fraction which occurred naturally in the crude oil. Because of this, thermal cracking was used extensively until the early 1940's. In 1936 a new process was introduced, catalytic cracking, which offered several advantages over the thermal process, both in gasoline yield and quality. Since then, the thermal cracking process has been almost entirely supplanted by the catalytic process (1,4). The catalytic processing of oil fractions involves the contact of the vapors with an acidic catalyst at high temperatures (about 500°C) for a few seconds at approximately atmospheric pressure.

Until very recently the catalysts commonly used in catalytic cracking were amorphous silica-alumina and some naturally occurring clays (3,4). Since 1964 new types of crystalline silica-alumina catalyst, called molecular sieves or zeolites, have largely replaced the less active amorphous materials (3).

One of the important characteristics of the catalytic cracking process is that the range of products obtained, and in particular the ratio
of gasoline to heavy fractions of liquid fuel, can be varied to satisfy the market requirements. Also, it is worth mentioning that light gases such as methane, ethane, and ethene are produced in small proportions only, in contrast with the substantially higher proportions of these compounds produced in the thermal cracking (1,4,7).

It is generally accepted that catalytic cracking involves the formation of surface carbonium ion intermediates and that these species undergo isomerization, cracking, hydrogen transfer, and alkylation reactions characteristic of homogeneous acid catalyzed reactions (1-12, 14-16, 18, 20). The nature of the surface active sites on which these ions are formed is not known with certainty. One suggestion is that such sites occur on silica-alumina catalysts as Al^3+:O:Si^4+ groups (3-9). In such groups, the aluminum atom is expected to have an activity characteristic of a Lewis-acid which in the presence of water converts into a Brønsted-acid, as illustrated below,

```
<table>
<thead>
<tr>
<th>Si-O-Al-O-Si-</th>
<th>+ H₂O</th>
<th>-&gt;</th>
<th>Si-O-Al-O-Si-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lewis-acid site</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Brønsted-acid site</td>
</tr>
</tbody>
</table>
```

Due to their crystalline nature and well-defined pore structure, the active sites in zeolites are believed to be more complex (5).

Since carbonium ions can undergo such a wide range of reactions, one might expect catalysts that form these intermediates to be rather non-selective. Such side reactions as isomerization, hydrogen transfer,
transalkylation of aromatics, cyclization, etc., may be expected as well as cracking. Some of these side reactions form higher molecular weight compounds and "coke" (3,4) which deactivates the catalyst. On the other hand, reactions like skeletal isomerization help to improve the quality of gasoline produced by cracking.

Industrially, the catalytic cracking operation takes advantage of the coke that is formed by burning it off in a regeneration step to provide heat for the endothermic cracking reaction (1,4,11). The most widely used process involves a fluidized-bed reactor (1). The cracking is carried out in a fluidized-bed reactor from which a portion of the catalyst is continuously removed and fed to another fluidized-bed regenerator where the coke is burned off. The regenerated catalyst is continuously returned to the cracking reactor. The heat requirements for the cracking reactions are provided by the heat of combustion of the coke, and is transferred to the cracking reactor by means of the hot, regenerated catalyst.

The coke formation is probably due to an excessive dehydrogenation of the hydrocarbon molecules. This naturally leads to a decline of the catalyst activity, but fortunately the carbon is readily removed by burning and the catalyst activity restored (3).

This study is concerned with the cracking or dealkylation of an alkylaromatic compound, iso-propylbenzene or cumene, viz

\[
C_6H_5 \cdot C_3H_7 \rightarrow C_6H_6 + C_3H_6
\]

It has been found (1) that benzene rings are not cracked and that side chains of alkylaromatics (where the alkyl group is C₂ or larger) are removed as olefins under the conditions normally used for this reaction.
(300° - 500°C, 1 atm).

The dealkylation reaction of cumene has been considered a model or test reaction for experimental purposes, since the only products obtained are benzene and propylene, i.e., there are no side reactions and it is essentially irreversible at atmospheric pressure in the temperature range of 300° to 500°C (3,4,7-11). Haensel (4) mentioned the reversibility of this reaction at low temperatures and high pressures over a silica-alumina-zirconia catalyst to produce mono- and di-iso-propyl-benzene, although at 400°C and atmospheric pressure and space velocity of 2 sec⁻¹, the equilibrium did not limit the dealkylation of n-butylbenzene.

Thus, the catalytic cracking of cumene to benzene and propylene takes place with minimal formation of by-products and is not affected by equilibrium limitations at moderate and high temperatures. Kinetic investigations are thus facilitated by the stoichiometric simplicity of the reaction and by neglecting the reverse reaction.

PREVIOUS WORKS ON SILICA-ALUMINA CATALYSTS

Thomas (9) and Greensfelder et al. (8) independently, but simultaneously, proposed chemical mechanisms for the cracking reactions of hydrocarbons over acidic silica-alumina catalysts. They postulated the formation of a carbonium ion at the surface of the catalyst, whereas thermal cracking was supposed to occur via free radicals. The kinetic scheme presented by these authors for the cracking of alkylaromatics can be illustrated by equations -1- to -3-.

\[
\begin{align*}
&\text{C}_6\text{H}_{13} + \text{H} + \text{catalyst}^\Theta \\
&\text{C}_6\text{H}_5^+ \quad \text{catalyst}^\Theta
\end{align*}
\]
Thomas (9) proposed that carbonium ions are formed by the addition of protons from the catalyst to a double bond in the benzene ring, thus forming a carbonium ion that decomposes at the beta position to the carbonium ion atom. This mechanism, however, assumes the addition to occur opposite to Markovnikov's rule, but in view of the resonating structure the departure from normal addition does not appear to be a crucial defect in the proposed mechanism.

Because of the great affinity of benzene rings for protons (as evidenced by the relatively easy deuterium exchange in the presence of an acidic catalyst) Greenfelder et al. (8) assumed that this first step in forming a carbonium ion is an exchange reaction wherein the benzene ring exchanges a carbonium ion for a proton. The extent of the dealkylation thus depends on the relatively ease of formation of the alkyl-carbonium ion. It is evident from the work of these authors that Brönsted acid sites should be responsible for the activity of the catalyst. Thomas (9) further showed that neither pure silica nor pure alumina has significant cracking activity.

Corrigan et al. (10) suggested that catalytic cracking of cumene proceeds by a surface reaction in which the cumene is chemisorbed on a
single active site, propylene is split off into the gas phase, and finally benzene is desorbed from the surface. Although these authors proposed a reasonable mechanism, their experimental work was shown by Pratter and Lago (11) to be affected by diffusional-transport limitations. Pratter and Lago (11) made an extensive review of the literature on the kinetics of cumene dealkylation published to that date (1956) and examined the previous investigation on the basis of the following points:

1. The use of a method insensitive to the kinetics,
2. the diffusion-transport effects, and
3. the presence of inhibitors in cumene.

They, in turn, postulated a basic kinetic scheme that took into account all these factors. Their kinetic reaction scheme involved the following:

1. Adsorption of cumene and inhibitors on active cracking sites follows a Langmuir type isotherm, i.e., there is little interaction among the chemisorbed species on the surface. In addition, they noted, the active sites are homogeneous with respect to adsorption energies.

2. The rate of cracking is proportional to the number of cumene molecules chemisorbed on active cracking sites.

Because their experimental conditions used a differential reactor (low conversion of reactants to products), they neglected the reverse reaction; hence, any possible effect that adsorption of products on the catalyst could have had on the adsorption of cumene. Their kinetic scheme is illustrated by Equation -4-,
where $A$ represents an active site; $S$ reactant cumene; and $I_i$ the $i$th inhibitor.

In the case of no inhibitors in cumene and assuming a Langmuir adsorption isotherm for the latter, the preceding scheme leads to the rate expression

$$\frac{dn}{dt} = k_B \frac{P_S}{3o P_S + G}$$

where $B_o$ is the total number of active cracking sites, $P_S$ is the partial pressure of cumene, and $G$ is a constant related to the chemisorption of cumene and is equal to $(k_2 + k_3)/k_1$.

Pratter and Lago found that the rate determining step is the cracking of the chemisorbed cumene (C-C bond rupture), characterized by $k_3$, if a linear relationship is to be held between $\ln G$ and $1/T$ (Arrhenius type relationship). Also, making use of absolute rate theory, under experimental conditions where $P_2 \gg G$, they obtained a formula for calculating the total number of active cracking sites $B_o$, viz,
\[ B_0 = 2.6 \times 10^6 \frac{h}{kT} \]

where \( k \) is the Boltzmann's constant and \( h \) is Plank's constant.

With regard to the coke formation on the surface of the catalyst, the authors proposed two different kinds of carbonaceous material:
1) strongly chemisorbed inhibitors not desorbed at the time of the shut-down operation for removal of the catalyst from the reactor, and
2) harmless carbonaceous materials which do not affect the catalyst activity. The materials in class 2 were referred to as coke by the authors. They sustained the hypothesis that cumene was not an important coke producer but the inhibitors were heavy coke producers which, by themselves, were responsible for the deactivation of the catalyst. Therefore, they concluded that coke was probably produced by a mechanism involving sites other than those active for cracking.

Horton and Maatman (12) studied the cracking of cumene over several impregnated and cogelled silica-alumina catalysts following the experimental indications outlined by Pratter and Lago (11) and applied the same kinetic scheme. They found differences between the impregnated catalysts and the cogelled catalyst, with the latter being more active although the number of active sites \( B_0 \), was lower than the \( B_0 \)'s for the impregnated catalysts. They explained this difference by postulating a qualitative dissimilarity between the sites in the impregnated catalysts and in the cogelled catalyst (having a higher percentage of Al). Therefore, they postulated, the reaction had to proceed by two different mechanisms on these catalysts: for the impregnated catalysts there should be one adsorption point in the active site, whereas for the cogelled catalyst there may be a high incidence of active sites involving two ad-
sorption points.

PREVIOUS WORK ON CATALYSTS OTHER THAN SILICA-ALUMINA

As mentioned earlier, the cumene cracking reaction has been used as a model for testing different catalysts and experimental procedures due to its simplicity. However, these studies were usually limited to the evaluation of a particular catalyst or technique and did not report other relevant information concerning the kinetics of the dealkylation process (21,22).

Over the last ten years a research group in the Department of Chemical Engineering at Queen's University in Kingston, Ontario, headed by B.W. Wojciechoski has reported interesting results about the catalytic cracking of cumene over a lanthanum-exchanged Y zeolite catalyst. In 1968, Wojciechoski (13) published his theory on the decay of activity of an aging catalyst. He assumed that catalyst activity is a function of the time on stream only, and on the basis of this assumption the behavior of fixed bed catalytic reactors was studied.

Most of the previous studies on cumene dealkylation reported an initial loss of activity, and kinetic results were reported after that initial loss. In practice, commercial catalysts are on stream for only about ten minutes and then require regeneration. However, the Wojciechoski group was interested in testing their theory with the known cumene dealkylation using this initial decay period.

Campbell and Wojciechoski (14) proposed a reaction mechanism for the cumene dealkylation reaction and later produced experimental results (15) to corroborate their mechanism. The Campbell and Wojciechoski mechanism is known as the "delta" (Δ) mechanism and it resulted from an ex-
pansion of the Pratter and Lago mechanism (11) when the reverse surface reaction is considered.

Due to the high degrees of conversion of cumene to products that can be achieved in an integral reactor, the reverse reaction (aklylation of benzene to cumene) needed to be considered, and it was assumed (11) that it requires the adsorption of either benzene or propylene on an active site followed by combination with the appropriate gas phase component by a Rideal mechanism. It was again considered that the adsorption of both cumene and one of the products follow a Langmuir adsorption isotherm. Furthermore, it was assumed that the rates of desorption of both cumene and the adsorbed product are fast compared with the rate of the surface reaction. Thus, equilibria are established between the gas phase species and their surface complexes. The mechanism proposed by Pratter and Lago (11) considering the back reaction is illustrated by Equation -7- and "inhibitors" are not considered in this case.

\[
\begin{align*}
&C + S \xrightleftharpoons[k_2]{k_1} CS \xrightarrow[k_3]{k_4} YS + Z \\
&\text{where } S \text{ represents an active site; } C, \text{ reactant cumene; and } Y \text{ and } Z, \text{ products.}
\end{align*}
\]

Campbell and Wojciechoski extended this mechanism to consider the more general case of adsorption of all components. The Δ mechanism can be illustrated by Equation -8-.
The model assumes that adsorption equilibria exist between C, Y, and Z and the active site S. Thus, the rate of disappearance of cumene, considering single site adsorption and the surface reaction as the rate determining step, is written as

\[- r_c = k_{-2}(CS) - k_2(YS)(Z) \]  

After substituting for (CS) and (YS) in terms of Langmuir isotherms, accounting for volume expansion of the products, for thermodynamic equilibrium, and for aging of the catalyst, the resulting rate equation was inserted into the design equation for a plug flow static reactor. The theoretical development led to Equation -10-.

\[ \tau (S_0) \left( \frac{1}{1 + G \tau} \right)^N = \frac{X_e^2}{k_2k_c} \left[ -pX + \frac{q}{2} \ln \frac{X_e^2}{X^2 - X} + \left( \frac{pX_e + s}{2X_e} \right) \ln \frac{X_e + X}{X_e} \right] \]  

where X is the instantaneous conversion of cumene on a catalyst of age t under conditions where the space time is \( \tau \) and the equilibrium fractional conversion is \( X_e \). The constants p, q, and s are referred to as kinetic parameters, and they involve adsorption equilibrium constants for C, Y, and Z. The constants N and G are aging parameters which relate the num-
ber of cracking sites or the number of surface sites, S, involved in the adsorption, \( n \), and the number of active sites lost per deactivating event, \( m \). The formulas for \( N \) and \( G \) are

\[ N = \frac{n}{(m-1)} \]

\[ G = (m-1)k_d[P] \]

\( k_d \) being the rate constant for the deactivation reaction, and \([P]\) conc of poisoning agent. These formulas and their derivation are given in (13) and they are part of the Wojciechowski's theory of catalyst aging. The values of the exponent \( N \) are determined from the deactivation pattern on a particular catalyst and in short three main classes of catalysts are found: for low decay \( N < 1 \); for limiting conversion \( N = 1 \); and for rapid decay \( N > 1 \).

As results of their study (15), Campbell and Wojciechowski reported an activation energy of 19.5 kcal and proposed propylene as the species responsible for deactivation of the catalyst by means of a polymerization reaction. They noted that for the La-exchanged zeolite catalyst the value of \( N = 1 \) was applicable. The deactivation process was concluded to proceed by a Hinshelwood mechanism.

The value of the activation energy obtained by these authors is lower than the change in enthalpy \( \Delta H \) for the reaction in the temperature range they worked in, suggesting that either the heat of adsorption of cumene is negative (an endothermic adsorption) or the reaction is diffusion limited in the crystallites of the zeolite.

Best and Wojciechowski (16) conducted a series of studies over La-exchanged zeolites of different particle sizes to determine the effect of intra-particle diffusion in an aging catalyst. As a result they in-
introduced a new test to evaluate the significance of intraparticle diffusion in the reaction (17). Using this test they showed that La-Y zeolite catalyst particles as small as 70-80 mesh were diffusion limited for cumene cracking. The activation energy obtained for the 70-80 mesh catalyst was somewhat larger (22.1 kcal) than that reported earlier by Campbell and Wojciechoski (15) for the same catalyst but with particles of 20-40 mesh size (mainly 19.5 kcal). This latter value of 22.1 kcal was in better agreement with other reported values over similar catalysts.

Based on adsorption and thermodynamic considerations, they found that if site poisoning is proceeded by a dimerization of an adsorbed species, cumene and not propylene (as previously proposed (15)) becomes the probable poisoning agent in the cumene cracking reaction. Also, it was found that coke on the catalyst is not directly related to catalyst activity.

In a more recent article, Best and Wojciechoski (18) published results of a more complete and detailed study of the cumene dealkylation. They observed that over 60 reaction products are formed over the La-Y zeolite. The selectivity behavior of the major ones (those which appear in concentrations higher than 0.01%) was examined using the concept of an "optimum performance envelope" (19) which is a curve obtained by plotting the time average yield of a reaction product versus the time average conversion of the reactant at a cat/oil ratio approaching infinity; in practice it is approximated by the data from runs at short times on stream for which the effects of catalyst decay are negligible. This selectivity behavior allows one to identify which products are primary and which are secondary and also those stable and those unstable. Based
on these observations, a reaction network was constructed. Chemical mechanisms by which primary products arise were postulated. They showed the competing influence of Brønsted and Lewis acid sites. In a later article (20) they succeeded in isolating the diffusion free region and determining the intrinsic kinetics. The activation energy reported for these conditions was 22.5 kcal. In analyzing the energetics of the reaction, they were forced to postulate an endothermic chemisorption of cumene in order to construct a plausible picture of the reaction energy surface. They also showed that diffusion limitations affected the rate of catalyst decay to a different extent than they affected the rate of reaction.

ISOTOPIC TRACER STUDIES

Studies (23-26, 38-41) using stable isotopic tracers (deuterium) have been performed on silica-alumina catalysts under a variety of conditions with several chemical systems. These studies had as goals the determination of hydrogen content of the catalyst, the existence of kinetic isotope effects and in general the search for evidence of protonic activity. The characterization of the chemical nature of the catalytically active sites on acidic catalysts has been the object of numerous papers spanning many years. The diverse results have led to the identification of Lewis acid, Brønsted, electron transfer, and perhaps other sites on these solids. However, no conclusive evidence about the predominance of one of those types on these catalysts has been reported. The possibility that different sites should be responsible for different reactions and that in some cases a combination of them could produce the desired catalysis, seems certain.
Silica-alumina, as other oxide catalysts, is able to catalyze exchange reactions (23-25). The study of exchange reactions provides a means of assessing the activity of catalysts for the making and breaking of chemical bonds and also results to be a good method of learning about adsorbed intermediates.

One of the first exchange reactions studied on silica-alumina catalysts was the exchange of CH$_4$ with CD$_4$ (26). The fact that exchange takes place shows that the catalyst is capable of breaking the C-H bonds. One alternative method to that of feeding a mixture of deuterated and non-deuterated reactants to a reactor containing the catalyst is to realize an exchange reaction involving the exchange of a hydrocarbon molecule with the catalyst. In this way the catalyst, for example, could be first deuterated and then another hydrocarbon molecule (similar or different to the original) could be passed over the catalyst to complete the exchange. Exchange reactions similar to self-exchange reactions, i.e., the exchange of CH$_4$ with CD$_4$ or C$_6$H$_6$ with C$_6$D$_6$, could be accomplished via deuteration of the catalyst. This case is considered to be one of the most satisfactory ways of investigating the exchange on oxide catalysts, and it is preferred over the deuteration of the catalyst with for example D$_2$ or D$_2$O. It has been found (27) that the exchange of C$_6$H$_6$ with C$_6$D$_6$ is approximately 10 to 20 times faster on alumina than exchange of C$_6$H$_6$ with D$_2$. Therefore, the self-exchange is probably more representative of the efficiency of the catalyst for activation of the benzene molecule. This difference is explained in terms of the significant inhibition of the H$_2$-D$_2$ exchange by benzene on alumina.

The extent of an exchange reaction will naturally depend on the
"strength" of the C-H bonds of the molecule. A hydrocarbon molecule such as an alkylaromatic will furnish a useful method to investigate the catalyst, because there are different types of C-H bonds present in the molecule which may exchange at different rates.

Considering the exchange reactions of alkylaromatics, important variations in the relative rates of exchange of side group and ring hydrogen atoms have been found (28). For example, for m-xylene, the ratio of ring to side group exchange varies from $10^{-1}$ on Palladium films to about $10^2$ on a silica-alumina catalyst.

As a general conclusion from studies on the exchange of alkylaromatics (25), it can be said that side group exchange is more rapid when radical intermediates are formed, as on metals or when dissociation occurs to form species with carbanionic character. Ring exchange is relatively faster on catalysts that can form carbonium ions readily (e.g., SiO$_2$-Al$_2$O$_3$, zeolites).

Galeski and Hightower (29) studied the cracking of cumene on a silica-magnesia catalyst by using deuterium tracers. They reported extensive exchange into the cumene prior to the dealkylation. Due to the fact that propylene, initially formed, was unexchanged they favored the classical ionic mechanism for the cracking (addition of a catalyst proton to the benzene ring). Data from studies of cumene cracking by Hightower et al. (30) over a deuterium exchanged silica-alumina catalyst under mild conditions (300°C, 10 psig) showed that benzene and propylene cracking products as well as unreacted cumene undergo rapid exchange with catalyst deuterium, so rapid in fact that the H and D atoms in the hydrocarbon molecule and catalyst are scrambled to statistical equilibrium.
The use of unstable (radioactive) isotopic tracers has been less extensive in the dealkylation reaction. Hightower and Emmett (31), in their study of the formation of aromatics during the cracking of n-hexadecane, used $^{14}$C-labeled benzene and ring labeled toluene to determine the extent to which the parallel steps of alkylation and combination of small unsaturated molecules to form benzene contributed to the formation of alkylaromatics. They found that the combination of propylene with benzene to form cumene was not notable.

**THERMODYNAMICS**

An analysis of the thermodynamic functions of the dealkylation reactants and products will give us a good idea of the enthalpy of reaction ($\Delta H$) involved and also of the reversibility of the reaction, at the temperature range under consideration in these studies.

As previously mentioned, cracking reactions are endothermic since they involve the cleavage of a carbon-carbon bond. Using the regular thermodynamic procedures and data from API Project 44, enthalpies of reaction, and standard chemical potentials, thermodynamic equilibrium constants are presented in Table I-1, at different temperatures, for the cumene cracking reaction.

The dealkylation reaction, due to its own endothermicity, will be thermodynamically favored at high temperatures and low pressures. Table I-2 shows the calculated equilibrium conversions at different temperatures as a function of the total hydrocarbon partial pressure at equilibrium.

**OBJECTIVES**

The purpose of this study was to determine the kinetic parameters
<table>
<thead>
<tr>
<th>t, °C</th>
<th>T, K</th>
<th>$\Delta H^\circ$, kcal/mole</th>
<th>$\Delta G^\circ$, kcal/mole</th>
<th>K, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>473</td>
<td>23.411</td>
<td>7.11</td>
<td>5.78 x 10^{-4}</td>
</tr>
<tr>
<td>250</td>
<td>523</td>
<td>23.274</td>
<td>5.41</td>
<td>5.48 x 10^{-3}</td>
</tr>
<tr>
<td>300</td>
<td>573</td>
<td>23.174</td>
<td>3.73</td>
<td>3.77 x 10^{-2}</td>
</tr>
<tr>
<td>350</td>
<td>623</td>
<td>22.997</td>
<td>2.03</td>
<td>1.94 x 10^{-1}</td>
</tr>
<tr>
<td>400</td>
<td>673</td>
<td>22.861</td>
<td>0.35</td>
<td>7.69 x 10^{-1}</td>
</tr>
</tbody>
</table>

$$K = \frac{P_{C_6H_6} P_{C_3H_6}}{P_{C_9H_{12}}}$$

$C_6H_5C_3H_7 \rightleftharpoons C_6H_6 + C_3H_6$

<table>
<thead>
<tr>
<th>Pressure, $P_0$ (atm)</th>
<th>Equilibrium fractional conversion, $X_e^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250°C</td>
</tr>
<tr>
<td>0.05</td>
<td>0.28</td>
</tr>
<tr>
<td>0.10</td>
<td>0.21</td>
</tr>
<tr>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>0.50</td>
<td>0.10</td>
</tr>
<tr>
<td>1.00</td>
<td>0.07</td>
</tr>
<tr>
<td>2.00</td>
<td>0.05</td>
</tr>
</tbody>
</table>
of the dealkylation reaction of cumene in a microcatalytic reactor system using the pulse technique. Furthermore, we sought to examine the possible influence that deposition of carbonaceous material on the surface of the catalyst might have on the kinetics of the reaction. Studies of exchange reactions with stable isotopic tracers were used to determine some characteristics of the catalyst and also a possible mechanism for the dealkylation reaction. Finally, part of this study dealt with the reversibility of the cracking reaction by use of radioactive tracers.

These studies were not designed to provide complete answers to all questions regarding interaction of hydrocarbons with acidic catalysts. We do feel however, that we have accumulated some important data that will shed insight into a few of the mechanistic details of those complicated reactions.
II. EXPERIMENTAL

CATALYST

The catalyst used for this study was commercial silica-alumina, SiO₂·Al₂O₃, Houdry M-46, with a composition of 12.5% alumina and having iron as the major metallic impurity amounting to about 0.1 to 0.3 wt% (32). Originally in the form of cylindrical pellets, the catalyst was ground and then sieved. Particles with 20-40 mesh size were selected for all experiments. The B.E.T. surface area of this catalyst, measured by adsorption of nitrogen at -195.6°C in a standard B.E.T. apparatus (33), was 278 ± 13 m²/gm. The bed density of the 20-40 mesh catalyst was 0.47 gm/cc as determined by measuring the volume occupied by a known weight of the solid in a 10 ml graduate cylinder.

Pretreatment of the catalyst was the same for all the kinetic and tracer experiments. It consisted of heating the catalyst overnight at 475°C in He flowing at 13.6 to 18.2 STP cc/min. The pretreatment of the catalyst for the deactivation studies was somewhat different and will be described later. The activity of the catalyst after regeneration in flowing He at 475°C was within 5% of the original activity for the fresh catalyst. This indicates that the catalyst used did not suffer any sintering. No further characterization of the catalyst was made.

CHEMICALS

The following chemicals were used in these studies:

iso-propyl benzene (Cumene), 99 mole percent minimum, from Aldrich Chemical Company, Inc.

Benzene, Spectroquality, from Matheson, Coleman, and Bell.
Ethyl benzene, 99 mole percent minimum, from Phillips Petroleum Company.

Benzene-d$_6$, minimum isotopic purity 99.5 atom % D, from Merck Sharpe and Dohme, Canada, Limited.

General purpose liquid scintillation counter cocktail, toluene based, Baker Analyzed Reagent grade, from J.T. Baker Chemical Company.

Benzene-$\text{^{14}C}$ was obtained from the dehydrocyclization of n-hexane $\text{^1}$$\text{^4}$C as described in (34) using a Tellurium loaded zeolite catalyst. The n-hexane $\text{^1}$$\text{^4}$C was obtained from American Radiochemical Company; its specific activity before dilution was 1 millicurie per millimole. Benzene-$\text{^{14}C}$ from American Radiochemical Company having a specific activity of 1 millicurie per millimole was later purchased for some of the experiments.

APPARATUS

**Microcatalytic Reactor and Gas Chromatograph**

The reaction system used in these studies is shown in Figure 1. It consisted mainly of a catalytic microreactor (29,30) coupled to a gas chromatograph that allowed analysis of the reaction products as well as the unconverted reactant.

The instrumental assembly can be described as follows: Helium (He) was used as the carrier gas and as the reference gas in the system. It exited from a pressure regulator at 10 psig and was divided into two branches with valves (V1) and (V2) being used to set the reference gas flow and the carrier gas flow, respectively. The reference He went
Figure 1. Instrumental Assembly
went directly into the thermal conductivity detector, TCD (D). The carrier gas line went to gas chromatograph oven (L). An injection port (IP) was used to introduce reactants to the system. Immediately downstream there was a four port valve (V3) that allowed the gas flow to by-pass the microcatalytic reactor. The by-pass operation permitted the use of the chromatographic system for calibration purposes or for collection and/or analysis of blank samples. The microreactor consisted of a glass tube (A), 1 cm I.D., where the catalyst was held between glass wool plugs. A pair of thermocouples (F) permitted control and measurement of the reaction temperature. A thermocouple well extended from the top of the reactor to about the middle of the catalyst bed. Two iron-constantan thermocouples were used, one for controlling and another for measuring the temperature. A Leeds and Northrup temperature controller maintained the temperature to within ± 1°C, as measured with a Leeds and Northrup potentiometer model #8686 and/or a double channel recorder.

After the reactor A and the valve V3, there was a product concentration trap (B) which essentially was a stainless steel U tube partially packed with small pieces of nichrome wire and wrapped externally with heating wire (H). This U tube, when kept submerged in liquid nitrogen (G), permitted the trapping of compounds coming from the reactor for the purpose of eliminating the dispersion effect that might have occurred in the catalyst bed, or to reset the appropriate conditions for the chromatographic analysis when these were different from those of the reaction, i.e., different volumetric flow for the carrier gas.

A 4-foot long, 1/4" OD, brass chromatographic column (C) packed in the laboratory with 10% SE-30 Silicone Rubber Gum on 60-80 mesh Chromosorb W AW was used for the analysis of the reaction products. This col-
umn could be by-passed by means of a valve (V4) for the purpose of obtaining different flow conditions (space times, \( \tau \)) in the catalytic micro-reactor. When this was done the product concentration trap B was kept submerged in liquid nitrogen G. Once the reaction was carried out at the desired flow rate, the column was placed back into the system, the analysis conditions reset, and the products trapped in trap B were flashed by means of an electronic timer-relay device that provided current to heater H for a short period of time. Thus, the chromatographic analysis was made in the normal fashion. When the flow conditions through the reactor were high (> 120 cc/min), the effectiveness of the trap B was not 100%. Under these conditions about 3% of the reactants was not trapped; the results were corrected for this ineffectiveness.

The thermal conductivity detector (D) was operated by a power source of regulated voltage built in the laboratory. The output was connected to a Perkin Elmer electronic integrator M-2 ("Minigrator") which in turn provided a signal to a double channel Hewlett Packard recorder model 7100-B. The recorder monitored the output of the TCD in one channel and the reaction temperature in the other.

At the exit of the detector D, in the carrier line, there was a 10/30 outer glass joint (I) to which a collection device could be attached. This allowed the collection of samples of individual compounds or groups of compounds for subsequent analysis with either the Mass Spectrometer, by means of sample tubes (J), or the Liquid Scintillation Counter for analysis of radioactivity, by means of vials for LSC, (K).

Additional accessories for this assembly were a fan for the chromatograph oven and thermometers for measuring the temperature in the column oven and in the detector oven.
The volumetric flows of He gas, in the reference as well as in the carrier streams, were measured by a soap-bubble flowmeter connected at the end of the reference and carrier gas lines.

Typical conditions of a chromatographic analysis are shown below:

Temperature of the chromatographic oven, \( T(\text{oven}) = 100^\circ \text{C} \).

Temperature of the detector oven, \( T(\text{detector}) = 125^\circ \text{C} \).

Flow (carrier) = 60 cc/min.

Flow (reference) = 60 cc/min.

Filament Current = 100 mA.

The temperature of the ovens was controlled by independent Variacs. Those portions of the carrier line after the column that were outside of the ovens were wrapped with heating wire and heated with independent Variacs.

Mass Spectrometer

The Mass Spectrometer used for the deuterium exchange experiments was a Consolidated Electrodynamics Corporation model 21-104 instrument. 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 the peaks were recorded on a Leeds and Northrup strip chart recorder. Samples were expanded from glass sample tubes, (I) in Figure 1, into a vacuum inlet system to provide a sample pressure of approximately 100 microns. The sample passed through a gold leak seal into the analyzer at a pressure of approximately \( 10^{-6} \) torr. Background pressure in the analyzer was of approximately \( 5 \times 10^{-8} \) torr.

Liquid Scintillation Counter

A Liquid Scintillation Counter model Unilux I fabricated by Nu-
clear Chicago was used to measure the radioactivity of the collected samples. The samples were changed automatically by the counter and every sample was counted for a lapse of time of 40 min. All the countings were made at room temperature.

EXPERIMENTAL PROCEDURES

Determination of Response Factors

A typical chromatogram of the products of the reaction of dealkylation showed the presence of at least four peaks. By measuring the retention times of pure compounds, these peaks were identified as being propylene, benzene, ethyl benzene and/or styrene, and iso-propyl benzene, as shown in Figure 2. Once these peaks were identified, the response factors of benzene, ethyl benzene, and cumene were determined by injecting different size pulses of the individual compounds and measuring their response. Calibration plots of the number of moles of the compounds versus the area obtained from the electronic integrator were used to establish the values of the response factors. These are as follows:

- Benzene \(2.6072 \times 10^{14}\) \(\mu\)moles/unit area.
- Ethyl benzene \(2.0803 \times 10^{14}\) \(\mu\)moles/unit area.
- Cumene \(1.8361 \times 10^{14}\) \(\mu\)moles/unit area.

These values, when multiplied by the appropriate areas obtained in a given run, gave the number of moles of each compound for that particular run. The response factor for propylene was not determined because its use was not necessary in calculating the conversion of reactant cumene. It should be noted that the peak corresponding to propylene might also contain small amounts of light gases such as methane and ethene. For the third peak in the chromatogram the designation of ethyl
Figure 2. Chromatogram of the products of the cumene dealkylation reaction.
benzene was adopted, and it was assumed that ethyl benzene and styrene have similar response factors. No other peak was detected after the cumene peak and for that reason the possibility of having di-iso-propyl benzene among the products of reaction was discarded.

Kinetic Experiments

Two different types of experiments dealing with the kinetics of the cracking reaction on silica-alumina catalyst were performed. Firstly, experiments in which the percent of conversion (% conv) of reactant cumene was measured as a function of the size of the injected pulse or number of moles of reactant injected at constant temperature, and secondly, experiments where the conversion of cumene was followed as a function of the absolute temperature. For this latter type of experiments the assumption of a first order rate dependence is made.

Constant Temperature Experiments

These experiments were performed to test the first order behavior of the dealkylation reaction. Essentially they were experiments in which the initial concentration of cumene was changed and the corresponding conversion to products monitored. These experiments were carried out at constant temperature and constant space time.

Pulses with size ranging from 4.0 to 0.5 μl of cumene were injected to the microcatalytic reactor system. Injections were made with a Hamilton microsyringe. Cumene was kept in a two-dram vial with a chromatographic septum held by a perforable cap. Several pulses of the same size were injected through the injection port and passed through the catalyst bed A having the valve V3 of the system in a position where the re-
actor was connected to it. Half a gram of the catalyst was used. The catalyst was pretreated as described previously. Trap B was kept submerged in liquid nitrogen and the products of reaction together with the unconverted reactant cumene were collected in this trap. After approximately 2 minutes, which was sufficient time for all the product molecules to be eluted from the catalyst bed at the carrier gas flow of 54.6 STP cc/min, the liquid nitrogen Dewar was removed from trap B and the heating wires H were turned on to flash the content of the trap into the chromatographic column for analysis.

After several pulses the conversion became almost constant and then the conversion readings of five consecutive pulses were averaged; that value was taken as the conversion for that pulse size.

**Variable Temperature Experiments**

These experiments were performed assuming that the dealkylation reaction followed an irreversible path and that it was first order with respect to reactant cumene with no change in the total volume, i.e., a constant density system.

The experimental procedure was quite similar to that for the experiments described in the previous section. The temperature of reaction was varied while the space time was held constant. Half a gram of catalyst was pretreated overnight as described earlier. Initially the temperature of the reactor was set at about 325°C and several pulses (2 µl) of cumene were passed over the catalyst at a space time of 1.0 sec. For each pulse the products coming out from the reactor were trapped in trap B and after 2 minutes flashed for chromatographic analysis. Injections of pulses of cumene were done until the conversion to products
showed a stable value, i.e., a plateau in the graph of % conv versus the pulse number. After this stable conversion was achieved, the temperature of the reactor was changed using the temperature controller. This temperature was continuously measured with the thermocouple F attached to a potentiometer. Thus, there was no need to wait for the temperature to reach a constant value since what was important was the value of the temperature when the pulse of cumene passed over the catalyst bed. Thus, when each 2 μl pulse of cumene was injected, valve V3 being in a position where the reactor was connected to the system, the temperature at that moment when the cumene passed through the reactor was recorded and the products of reaction were collected in the liquid nitrogen trap B. Again, after 2 minutes the liquid nitrogen Dewar was removed and the products were flashed for chromatographic analysis.

The carrier gas (He) flow for these experiments was set at 60 cc/min (measured at room temperature) and the chromatographic conditions were those given before.

The reactant cumene used for the variable temperature experiments was bought from Aldrich Company, but one experiment was carried out using cumene that had been stored in contact with activated charcoal.

The temperature ranged between 250°C and 400°C, and about 10 to 20 pulses of cumene were injected in a single experiment depending on the specific temperature range for a given run.

**Deactivation Experiments**

The study of the decay of the catalyst activity was carried out with an experimental procedure similar to the kinetic experiments described in the previous sections. Usually, pulses (2 μl) of cumene
were injected into a stream of He flowing at 60 cc/min (measured at room temperature) and at a given temperature of reaction. After passing through the reactor, the products were trapped in liquid nitrogen and then flashed for chromatographic analysis.

The main variables used in these studies were the reaction temperature, the catalyst pretreatment, and the reactant purity, as we monitored the change in cumene conversion as a function of the number of pulses passed over the catalyst in each case.

For the experiments where the effect of possible inhibitors of the reaction was to be studied, the pretreatment of the catalyst was different from that described before. After leaving the catalyst overnight at 475°C in He flowing at 18 STP cc/min, a flow of 11 STP cc/min of oxygen was passed over the catalyst for two hours at 450°C. In order to proceed in this manner, the column C was by-passed using valve V4 and the detector D disconnected from the system. The reactant cumene, for this same purpose, was "purified" in the following ways:

a) "Distilled cumene": Reactant cumene was distilled under vacuum and used right after distillation. A standard micro-distillation set was used for this purpose.

b) "Cumene on outgassed activated charcoal": Activated charcoal was outgassed overnight at 200°C and reactant cumene was poured into the sample tube containing the charcoal. A rubber septum was placed on the tube and samples for reaction were taken as normal.

c) "Cumene on charcoal": Activated charcoal that had not been outgassed was placed in a bottle and cumene poured into it.

For every experiment 10 or more pulses were passed over the catalyst.
Since a sample of catalyst could have lost some activity due to sintering during these reactions, the B.E.T. surface area for a catalyst sample under such circumstances was measured. A value of 278 m²/gm was obtained. This value is similar to the surface area for the fresh catalyst.

**Isotopic Tracer Experiments**

In order to know the details of the mechanism of the dealkylation reaction, isotopic tracer experiments were performed using deuterium in per-deuterated benzene as the deuterating agent for the catalyst.

A catalyst sample (0.5 gm of SiO₂-Al₂O₃) was deuterated by passing over it pulses of C₆D₆; the cumene dealkylation reaction was then carried out over this catalyst. The analysis of the relative content of deuterium in benzene was made in the mass spectrometer after chromatographic separation. For this purpose a sample tube J, shown in Figure 1, was connected to the system at I.

After pretreating the catalyst, two blank samples of perdeuterated benzene, C₆D₆, and regular benzene, C₆H₆, were injected by-passing the reactor with valve V3. The compounds were collected in the sample tube J submerged in liquid nitrogen. This sample tube was previously evacuated and thawed at least twice for assurance of no contamination. The sample tube was connected to J by means of a glass joint 10/30. The other end of the tube had a 12/30 inner joint that allowed one to evacuate the inert gas and introduce the samples into the mass spectrometer. The blank samples were analyzed to obtain the correction factor due to natural occurrence of ¹³C in hydrocarbons as well as to know the exact position of the ion-molecules of these species.

Once this was done, six consecutive pulses of C₆D₆ were passed over
the catalyst, each collected in the sample tubes and analyzed for the relative amounts of the different deuterated species of benzene. The inert gas trapped in the sample tubes at liquid nitrogen temperature needed to be evacuated and the sample thawed before introduction of about 100 microns of sample into the spectrometer.

Immediately after, six consecutive pulses of cumene were passed over the deuterated catalyst surface, and the same procedure of trapping the products and subsequent flashing for chromatographic analysis was followed. After chromatographic separation, benzene was collected in the sample tubes for mass spectroscopic analysis. For some experiments the unconverted cumene was also collected in a separate sample tube. In these cases, benzene and propylene were collected together in a sample tube.

In order to collect the unconverted cumene, free of benzene, a 3-way valve (V5) and a double branched exit was used, as shown in Figure 3. The carrier gas line after the detector and up to the exit ports was kept warm with heating wires and tapes to avoid condensation of the chemicals. The sample tubes, previously evacuated, were connected to the ports. One of the sample tubes was closed while the other was filled with He for about 2 minutes. After this time, the stopcock of this sample tube was closed, valve V5 switched, and the stopcock of the other tube opened. Then, liquid nitrogen Dewars were placed and the same procedure of sweeping the sample tubes with Helium was carried out. Whenever a pulse of cumene was passed over the catalyst, one sample tube was open to ventilation (He flowing through it) and this tube was used to trap propylene and benzene. When the first sign of the cumene peak was observed in the
Figure 3. Scheme for the collection of benzene-propylene and cumene peaks for Mass spectroscopic analysis.

Figure 4. Chromatogram indicating switching of V5 for collection of cumene.
chromatogram, valve V5 was switched and the stopcock of the tube to collect cumene was opened while the other one was closed. Figure 4 shows a chromatogram indicating the switching of the valve.

This procedure, besides assuring a minimum of benzene in the collected cumene, also allowed a minimum of air in the sample tubes.

The isotopic tracer experiments were performed at several temperatures and the space time was kept constant, namely, 1.0 sec measured at room temperature.

**Radioactive Tracer Experiments**

Radioactive tracer experiments with $^{14}$C were done to determine if the dealkylation reaction showed any indication of reversibility in the temperature range from 300°C to 400°C. To perform this task, mixtures of benzene-$^{14}$C and cumene were prepared beforehand and injected into the reactor. The radioactivity of product benzene and unconverted cumene was measured and the values plotted as a function of the degree of conversion at different space times. The starting mixture contained a ratio of approximately 4:1 by volume of cumene to radioactive benzene.

In each series of experiments, this mixture was injected into the system at a constant reaction temperature but at different space times to obtain different degrees of conversion of cumene. A series of experiments were carried out at four different temperatures.

In order to measure the radioactivity of the compounds with the Liquid Scintillation Counter, the individual compounds (benzene and cumene) had to be collected in a counting medium, a liquid scintillation cocktail. For this purpose, vials containing 17 ml of this cocktail were kept at a temperature just below 0°C in a salt-ice bath. The vials
were attached to the system through the collection device I shown in Figure 1. The hydrocarbons were quantitatively dissolved in the scintillation cocktail.

Experimentally, the space time was varied first by disconnecting the column C shown in the instrumental assembly, Figure 1; this could be done by opening completely V4. The carrier gas flow was then set at the desired value using the needle valve V2. The resulting flow was measured with a soap-bubble meter at room temperature.

With the desired flow rate set, a pulse of the mixture was injected and passed over the catalyst. The products were trapped in liquid nitrogen (trap B), this time with a double purpose: first, to eliminate the partitioning effect that the solid catalyst could have had on the compounds and secondly, to restore the appropriate carrier flow rate for the chromatographic analysis. Likewise, the column C was placed back into the system by shutting off valve V4. The products were then flashed, separated, and analyzed in the chromatograph. Benzene and cumene peaks were collected in the Liquid Scintillation vials as they eluted from the system. The difference in the retention times between benzene and cumene peaks allowed the vials to be changed without losing any products.
III. RESULTS

DEACTIVATION MEASUREMENTS

If several pulses of cumene were passed over a fresh sample of catalyst that had been activated in He flow at 475°C overnight, the activity (measured as conversion of cumene to products) decreased markedly at the beginning.

Figure 5 shows the decrease in the degree of conversion of cumene to products at several reaction temperatures when plotted against the pulse number, PN. Several features can be noted from these results: First, we note that the decay of the catalyst activity is present at all temperatures in the range studied (250° to 350°C); secondly, although the initial decrease in the degree of conversion is lower at lower temperatures, this initial decrease seems to follow a rate equation which is first order with respect to the initial activity \( X_0 \), viz,

\[
- \frac{dX}{d(PN)} = kX_0^n
\]

or in its linear form

\[
\ln \left( - \frac{dX}{d(PN)} \right)_T = \ln k + \ln X_{0,T}
\]

if \( n = 1 \). Figure 6 shows a plot of \(-\ln(-dX/dPN)\) versus \(-\ln X_{0,T}\) and the data points fit very well a straight line with slope close to unity.

The initial slopes of the deactivation curves were determined by two different methods: the approximation method and the limiting secant method, both described in (36). Equation -13- implies that \( k \) is not a function of temperature, since \( X \) was varied by changing \( T \).

The data obtained from both methods were fitted to a straight line
Figure 5. Decay of activity with pulse number.

Figure 6. First order decay plot.
by the least squares method, and the two resulting values of the slope of \( \ln (\frac{-dX}{dPN}) \) versus \( \ln X_0 \) were

\[
n = 0.9 \pm 0.2
\]

In Figure 6 the data points obtained from the limiting secant method are plotted against \( \ln X_0 \). Even though catalyst deactivation was observed initially at all temperatures, the conversion tended to become relatively stable after about 15-20 pulses were injected. Of course, this observation is in disagreement with the empirical Equation -13- which predicts a continuous decrease in conversion with pulse number with the limiting conversion being zero for an infinite number of pulses at each temperature.

All the kinetics measurements discussed herein were taken on a catalyst that had been deactivated to a relatively stable activity level. This is referred to as a "stabilized" catalyst.

Figure 7 shows the effect that impurities in reactant cumene could have inhibiting the dealkylation reaction. It was assumed that if impurities were present in the starting material, they would adsorb on the charcoal used in these experiments or be separated from cumene through vacuum distillation. All runs were made at 300°C. For these experiments, the first point was always taken with "distilled cumene" to serve as a reference point. It can be noted in the figure that within the experimental error (shown by the scattering for the first point) all the points approximately lie on the same curve, indicating that there is no significant difference between the various "kinds" of cumene used.

However, Figure 8 shows that for long runs (thirty or more pulses)
Figure 7. Effect of "inhibitors" on the catalyst activity.
Figure 8. Effect of the reactant impurities on the catalyst activity during long runs.
there is an appreciable difference between the decay of the catalyst activity when "distilled cumene" is used and the decay when untreated cumene is used. It should be pointed out here that a mass spectrum of cumene at nominal ionizing voltages of 5 and 10 volts did not show m/e peaks above the m/e value corresponding to 120, the molecular weight of the cumene ion-molecule.

Since most of the experiments performed in this thesis work did not require a large number of pulses, regular (or untreated) cumene was normally used.

Finally, Figure 9 shows the decay of the activity of the catalyst as a function of the pulse number together with the total number of μ-moles of products recovered. Also, the accumulated number of μ-moles of reactant lost over a span of thirty pulses is plotted against the pulse number.

The number of moles of product recovered is defined as:

\[ n_{\text{total}} = n_{\text{Bz}} + n_{\text{EtBz}} + n_{\text{Cu}} \]  

The number of moles of cumene lost is defined as:

\[ n_{\text{lost}} = n_{o} - n_{\text{total}} \]

\[ n_{o} \] being the number of moles of reactant cumene in every pulse, \[ n_{o} = 14.34 \] μ-moles of cumene (2.0 μl).

From this figure we can observe that the accumulated number of moles of reactant cumene lost tends to a steady value as does the degree of conversion. On the other hand, the number of moles of reactant lost seems to approach zero (or a very small value) as the number of moles recovered,
Figure 9. Relationship of % conv. ○; number of moles recovered, \( n(\text{total}) \Delta \); and accumulated number of moles lost, \( n(\text{lost}) \square \), with the pulse number for the cumene cracking over Si0-Al₂O₃ at 305 °C.
n_{total}, approaches the number of moles injected, n_o.

KINETIC MEASUREMENTS

**First Order Kinetics**

It has long been stated that the dealkylation reaction of cumene follows a first order kinetics having as reaction products benzene and propylene (3,10). Our first task in this part of the study was to test the assumption of first order with respect to the reactant cumene.

If a chemical reaction has a rate expression as

\[
\text{rate} = k C
\]

where the concentration of the reactant C can be related to its initial concentration C_o and fractional conversion X, viz,

\[
C = C_o (1 - X)
\]

or

\[
X = 1 - \frac{C}{C_o}
\]

the fractional conversion should be independent of the initial concentration or the pulse size used in a system like ours. It should be a function only of the temperature and space time, \(\tau\).

Figure 10 is a plot of percent conversion (100X) against the amount of cumene injected in \(\mu\)l and \(\mu\)-moles, at two different temperatures for low (275°C) and high (325°C) conversion ranges.

The percentage of conversion is almost independent of pulse size, but not exactly. Therefore the assumption of first order kinetics is not completely valid, although it represents a fairly good approximation.
Figure 10. Test for first order kinetics.
Kinetic Parameters for the First Order Approximation

If we assume that the cracking reaction is first order, irreversible, and occurs at constant density, we can derive a mathematical equation that will allow us to calculate the Arrhenius parameters for the cumene dealkylation reaction over silica-alumina.

Let us assume that the rate of dealkylation can be described by

\[- \frac{dp}{d\tau} = kp\]

where $p =$ partial pressure of cumene, (torr)

$k =$ pseudohomogeneous rate constant, (sec^{-1})

$\tau =$ space time $= V_{\text{cat}}/Q_{o}$, (sec)

$Q_{o} =$ volumetric flow rate, (cc/sec, measured at room temperature)

and $p = P_{o}(1-X)$

$X =$ fractional conversion,

then

\[\frac{dX}{d\tau} = k(1-X)\]

integration of this equation, with boundary conditions $X = 0$ at space time $\tau = 0$, yields

\[\ln \frac{1}{(1-X)} = k\tau\]

If we now express the rate constant in the form of an Arrhenius equation

\[k = Z\tau \exp(-\frac{E_{\text{act}}}{RT})\]

and plug it into the integrated rate expression given above, we end up with

\[\ln \left( \frac{1}{(1-X)} \right) = Z\tau \exp(-\frac{E_{\text{act}}}{RT})\]

or
\[
\ln \left[ \ln \left( \frac{1}{(1-X)} \right) \right] = \ln Zr - \frac{E_{\text{act}}}{RT}
\]

We note that a plot of \( \ln \left[ \ln \left( \frac{1}{(1-X)} \right) \right] \) against \( 1/T \) should be a straight line with slope of \( -\frac{E_{\text{act}}}{R} \) and intercept equal to \( \ln Zr \).

Figure 11 shows the Arrhenius plot for the dealkylation reaction when propylene and benzene are the only products considered. The fractional conversion for this case was defined as

\[
X = \frac{\text{moles Bz}}{\text{moles Bz} + \text{moles Cu}}
\]

The volumetric flow rate \( Q \) for this experiment was 60 cc/min (measured at room temperature), and the volume of the catalyst was taken as 1 cc giving a space time \( \tau = 1.0 \) sec.

The values of the apparent activation energy and of the preexponential factor determined by linear regression of the data are

\[
E_{\text{act}} = 14.8 \pm 0.9 \text{ kcal mole}^{-1}
\]

\[
Z = 0.77 \times 10^{5} \text{ sec}^{-1}
\]

therefore

\[
k = 0.77 \times 10^{5} \exp\left( -\frac{7436.3}{T} \right) \text{ sec}^{-1}
\]

Figure 12 also shows an Arrhenius plot for the dealkylation reaction, but in this case propylene, benzene, and ethylbenzene were considered as products of reaction. The fractional conversion in this instance was defined as

\[
X = \frac{\text{moles Bz} + \text{moles EtBz}}{\text{moles Bz} + \text{moles EtBz} + \text{moles Cu}}
\]
Figure 11. Arrhenius plot for the cumene dealkylation. Propylene and benzene as products.
Figure 12. Arrhenius plot for the cumene dealkylation. Propylene, benzene and ethyl benzene as products.
The conditions of \( Q_0 \) and \( V_{\text{cat}} \) were the same and the values obtained for \( E_{\text{act}} \) and \( Z \), determined also by linear regression of the data, are

\[
E_{\text{act}} = 15.1 \pm 0.9 \text{ kcal mole}^{-1}
\]

\[
Z = 2.12 \times 10^5 \text{ sec}^{-1}
\]

Therefore

\[
k = 2.12 \times 10^5 \exp\left(-\frac{7587.3}{T}\right) \text{ sec}^{-1}
\]

The difference in the values of the Arrhenius parameters is not really significant and might very well be within the experimental error. The preexponential factor is obtained from the intercept, which involves extrapolation of the data over a long distance and is subject to considerable uncertainty.

In order to look a little deeper into the effect of considering other reaction products besides propylene and benzene, Figure 13 shows the product distribution with temperature for the dealkylation reaction. It can be seen that the amounts of ethyl benzene (and/or styrene, see page 26) are really negligible when compared with the produced amounts of benzene. Another interesting feature to be pointed out here is that while benzene starts forming at temperatures below 250°C, ethyl benzene is not formed appreciably until after 300°C.

Since a catalytic reaction can operate under many and varied conditions, it is expected that these conditions can affect the mode of transport of the gaseous molecules through a porous structure, as is the case with silica-alumina. In the steady state, all steps in the series (be they transport, chemical reaction, etc.) occur at the same rate. This does not mean that one step may be, in fact, the rate limiting
Figure 13. Product distribution with temperature.
step. Thus, when the situation is that the "ease" of transport of the
gaseous molecules is comparable with the "ease" of the surface chemical
reaction, the observed kinetics may be influenced by both phenomena. It
is therefore pertinent to consider them both and to examine the possibil-
ity of being under a diffusion controlled regime.

For the case of a porous catalyst, intraparticle diffusion is usually
one of the factors to be considered and the criterion to discard diffusion
effects is based upon (11,35)

\[
\frac{dn}{dt} \cdot \frac{1}{c} \cdot \frac{R^2}{D_c} = \frac{R^2k}{D_c} \leq 1
\]

where in our case, \( \frac{dn}{dt} \) is the rate of cracking per unit volume of cata-
lyst, in (moles/cm\(^3\) sec)

\( c \) is the concentration of reactant, in moles/cm\(^3\)

\( R \) is the catalyst particle radius, in cm

\( D_c \) is the effective diffusivity of cumene in the porous
catalyst particle at the temperature of reaction, in cm\(^2\)/sec.

This criterion can also be stated in terms of the Thiele-like modul-
us for spherical particle for a first order reaction, viz,

\[
\phi_s = R^2 \left( \frac{k}{D_c} \right) \leq 1
\]

Such values of the Thiele-like modulus for spherical particles will
render an effectiveness factor value of \( n=1 \), meaning no diffusion con-
trol.

To calculate \( \phi_s \) we need to know the values of \( D_c \), the effective dif-
fusivity of cumene and the catalyst particle radius. \( D_c \) can be calcu-
lated from (11)
\[ D_c = D_{H_2} \left( \frac{M_{H_2}}{M_C} \frac{T}{T_0} \right)^{\frac{1}{2}} \]

if the effective diffusivity of \( H_2 \) is known. Pratter and Lago (11) measured \( D_{H_2} \) in a similar catalyst at \( T_0 = 300°K \) and obtained \( D_{H_2} = 7.0 \times 10^{-3} \text{cm}^2/\text{sec} \). Plugging in the values for the molecular weights of \( H_2 \) and cumene we get a value for \( D_c = 1.25 \times 10^{-3} \text{cm}^2/\text{sec} \) at \( T = 573 \text{K} \) (300°C).

The radius for the catalyst particles is obtained from the mesh size; thus,

<table>
<thead>
<tr>
<th>Mesh size</th>
<th>( \mu m )</th>
<th>Diameter, cm</th>
<th>( R, \text{ cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>850</td>
<td>0.0850</td>
<td>0.0425</td>
</tr>
<tr>
<td>40</td>
<td>425</td>
<td>0.0425</td>
<td>0.0213</td>
</tr>
</tbody>
</table>

Using these values and that of the corresponding to the rate constant at 300°C, \( k = 0.3764 \text{ sec}^{-1} \), we get

\[ \phi_s = 0.5439 \text{ for 20 mesh size,} \]
\[ \phi_s = 0.1366 \text{ for 40 mesh size.} \]

Using a plot of \( n \) versus \( \phi_s \) for the isothermal case of a first order reaction in sphere (35) we readily see that \( n \) is very close to unity indicating that no diffusion limiting factors are predominant.

So far we have worked with the so-called pseudohomogeneous rate constant \( k \), which may be influenced by diffusional limitations. However, now that we know diffusion effects are not limiting the rates, we can calculate the first order rate constant for the dealkylation reaction, \( k_s \), from either the extensive rate equation

\[ \text{rate} = k_s \text{ S.A. p_C} \]

where S.A. is the surface area, in cm²,
or the intensive rate equation (per unit reactor volume)

\[ r_c = k_s \left( \frac{S.A.}{\text{reactor volume}} \right) p_c = k_p c \]  

The reactor volume can be obtained from the bed density \( \rho_B \) (measured as described in the experimental part) and the weight of the catalyst sample, so, reactor volume = 1.064 cm\(^3\).

Thus,

\[ k_s = \frac{k \times \text{reactor volume}}{\text{S.A. for 0.5 gm of catalyst}} \]

\[ k_s = \frac{0.3764 \text{ sec}^{-1} \times 1.064 \text{ cm}^3 \times 2}{278 \times 10^4 \text{ cm}^2} \text{ at 300°C.} \]

\[ k_s = 2.88 \times 10^{-7} \text{ cm/sec} \]

DEUTERIUM TRACER EXPERIMENTS

The object of these experiments was to determine the number of hydrogen atoms on the catalyst surface by exchange with deuterium atoms in C\(_6\)D\(_6\), and to study the details of the exchange of cumene with a partially deuterated catalyst as a way to find out some information about the mechanism of this cracking reaction.

Mass spectrometric analysis of the reaction product, benzene, provided a measurement of the mole fraction, \( d_1 \), of the hydrocarbon containing \( i \) deuterium atoms per molecule, i.e., the relative content of each isotopic species C\(_6\)D\(_5\), C\(_6\)HD\(_5\), C\(_6\)H\(_2\)D\(_4\), etc. This is based upon the fact that when benzene was passed over the catalyst at the temperature range studied (300° to 380°C), there was apparently no chemical reaction, as only one peak was observed on the chromatogram. Similarly, when perdeuterated benzene (C\(_6\)D\(_6\)) was injected only one GLC peak was observed,
but mass spectral analysis of that benzene peak revealed that extensive exchange had occurred between the catalyst hydrogen atoms and the hydrocarbon deuterium atoms.

By comparing the isotopic distribution in the benzene product with that of the starting material, one can calculate the number of H or D atoms which underwent exchange during the reaction. For example, the average number of atoms exchanged by a heavy (perdeuterated) molecule with a catalyst surface originally containing no deuterium atoms can be determined from the following equation (29,30)

\[ \phi = \frac{\text{atoms exchanged}}{\text{molecule}} = \frac{n}{\sum_{i=0}^{n-1} (n-i)d_i} \]

where \( n \) is the total number of (hydrogen + deuterium) atoms in the molecule. A similar equation exists for exchange into a molecule originally containing no deuterium atoms, interacting with a deuterated catalyst surface, viz,

\[ \phi = \sum_{i=0}^{n} i d_i \]

Thus, mass spectrometric analysis of benzene provides a measure of the relative content of the different isotopic species after interaction with the catalyst; the value of \( n \) in the above equation is equal to six. Due to natural occurrence of \(^{13}\text{C}\) in hydrocarbons, a correction of the raw mass spectra result had to be made.

The first step in our experiments was to deuterate the catalyst using for this purpose \( \text{C}_6\text{D}_6 \). After initial deuteration of the catalyst surface (partial deuteration by injection of six pulses of \( \text{C}_6\text{D}_6 \)), the cracking reaction of cumene was carried out over this catalyst (inject-
ion of six pulses of \( \text{C}_6\text{H}_{12} \) and a similar analysis of the benzene product was performed in the Mass Spectrometer.

Figure 14 shows the deuterium distribution in benzene after exchange of the D atoms in six successive pulses of \( \text{C}_6\text{D}_6 \) with the H atoms on the surface of the catalyst. In this figure the theoretical values for the exchange, obtained by assuming a statistical binomial distribution of deuterium, are represented by solid lines; experimental data points are also shown. The extensive degree to which the exchange occurred during the deuteration of the catalyst is evident. Figures 15 to 17 show the distribution in benzene after passage of each individual pulse of \( \text{C}_6\text{D}_6 \), and the theoretical binomial distribution for each one is also presented. The binomial distribution was calculated from

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

where \( f(x,n,\theta) \) is the probability of exactly \( x \) successes in \( n \) independent binomial trials with probability of success on a single trial equal to \( \theta \).

In our case, we identify \( x \) with \( i \), \( i = 0,1,2,...,n \); \( n=6 \) the total number of hydrogen atoms in the benzene molecule; and \( \theta \), the probability of success on a single trial is related to the mean of a binomial expansion by the equation

\[
\text{mean} = \phi = n\theta
\]

\( \phi \) being the average number of atoms exchanged.

When \( \text{C}_6\text{D}_6 \) is injected, the first term in the binomial expansion \( (x = 0) \) will correspond to no success and it will give the fraction of the \( \text{d}_6 \) species, i.e., no deuterium exchange. Consequently, the last term of the expansion \( (x = 6) \) will correspond to \( \text{d}_0 \) or all deuterium
Figure 14. Deuterium distribution in benzene versus the reciprocal of the pulse number, after deuteration of the catalyst. Solid lines: theoretical values from the binomial equation. Experimental points are shown and were taken at 598 °K.
Figure 15. Deuterium distribution in benzene after passage of the first and second pulses of C.D. over the silica-alumina catalyst at 598 °K. Solid lines: experimental. Dashed lines: theoretical binomial distribution.
Figure 16. Deuterium distribution in benzene after passage of the third and fourth pulses of C₆D₆ over the silica-alumina catalyst at 598 °K. Solid lines: experimental. Dashed lines: theoretical binomial distribution.
Figure 17. Deuterium distribution in benzene after the passage of the fifth and sixth pulses of C₆D over the silica-alumina catalyst at 598 °K. Solid lines: experimental. Dashed lines: theoretical binomial distribution.
atoms exchanged. If we were to start with a nondeuterated species, i.e., 
C\textsubscript{6}H\textsubscript{12} used for the last six pulses, the situation would be reversed. In summary we can write equations for the binomial distribution depending on the injected species as follows

\[ f(i,6,\phi/6) = \binom{6}{i} (\phi/6)^i (1-\phi/6)^{6-i} \]

for injection of C\textsubscript{6}H\textsubscript{12}, and

\[ f(i,6,\phi/6) = \binom{6}{i} (\phi/6)^{6-i} (1-\phi/6)^i \]

for injection of C\textsubscript{6}D\textsubscript{6}.

For all the pulses injected, either C\textsubscript{6}D\textsubscript{6} for the deuteration of the catalyst or C\textsubscript{6}H\textsubscript{12} for the exchange during cracking, a parameter \( \Sigma \) which measures the cumulative number of atoms exchanged was obtained from

\[-44- \text{ in the case of injection of C}_{6}D_{6}, \text{ and } -45- \text{ in the case of injection of C}_{6}H_{12}.\]

\[
\text{total \# atoms exchanged} \text{ over the number of pulses injected.}
\]

\[-45- \text{ where } \Sigma \text{ measures the cumulative number of atoms (or surface atoms) exchanged when cumene was injected, a factor of 2 appears. This is so because of our assumption that cumene suffered the same type of exchange as benzene did, namely, rapid exchange or scrambling until statistical equilibrium. Now, benzene, which was the compound analyzed for deuterium content, contains only half the number of hydrogen atoms.} \]

[Image 0x0 to 576x768]
as cumene. Table III gives results to support this approximation, and later in the text we will treat this subject in more detail.

Tables IV to VII show the results for the deuteration of the catalyst, and Tables VIII to XI give the results for the recovery of deuterium from the catalyst surface when the cracking reaction was carried out. The inverse of the cumulative number of surface atoms (H or D) exchanged, $1/E$ is also tabulated. The significance of this parameter arises from the assumption that exchange reactions are considered reversible and that the exchange equilibrium is achieved for each pulse. A linear relationship between $1/FN$ and $1/E$ allows one to determine the total number of H atoms on the surface of the catalyst, and also the number of D atoms that can be recovered from the surface (see Appendix I). The deuterium exchange experiments were carried out at four different temperatures.

Figures 18 to 25 show the average number of atoms exchanged per molecule, $\phi$, and the cumulative number of H or D atoms exchanged between the catalyst and the hydrocarbon after passage of successive pulses of $C_6D_6$ and cumene over the catalyst at the four different temperatures used.

Figures 26 and 27 show the linear plots of the reciprocal of the cumulative number of atoms exchanged and the inverse of the pulse number at the four temperatures for the cases of injection of pulses of $C_6D_6$ and $C_9H_{12}$, respectively. This linear relationship is demonstrated in Appendix I, and the values of $1/E_o$ were calculated by linear regression fitting of the data.

Taking cognizance of the magnitude of the experimental and extrapolation errors involved in the calculations of the values of the recipro-
TABLE III
Isotopic Composition of Products in Microcatalytic Tracer Experiments

<table>
<thead>
<tr>
<th>PN²</th>
<th>Injected species</th>
<th>Measured species</th>
<th>d₀</th>
<th>d₁</th>
<th>d₂</th>
<th>d₃</th>
<th>d₄</th>
<th>d₅</th>
<th>d₆</th>
<th>d₇</th>
<th>d₈</th>
<th>d₉</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>0.03</td>
<td>0.10</td>
<td>0.20</td>
<td>0.24</td>
<td>0.19</td>
<td>0.10</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td>2.70</td>
</tr>
<tr>
<td>2</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>0.01</td>
<td>0.04</td>
<td>0.12</td>
<td>0.24</td>
<td>0.30</td>
<td>0.23</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td>2.21</td>
</tr>
<tr>
<td>3</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>--</td>
<td>0.01</td>
<td>0.05</td>
<td>0.16</td>
<td>0.29</td>
<td>0.32</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>--</td>
<td>--</td>
<td>0.02</td>
<td>0.10</td>
<td>0.25</td>
<td>0.38</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>--</td>
<td>--</td>
<td>0.01</td>
<td>0.06</td>
<td>0.18</td>
<td>0.40</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>C₆D₆</td>
<td>Bz</td>
<td>--</td>
<td>--</td>
<td>0.01</td>
<td>0.04</td>
<td>0.15</td>
<td>0.38</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
<td>0.82</td>
</tr>
<tr>
<td>7</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.15</td>
<td>0.29</td>
<td>0.28</td>
<td>0.17</td>
<td>0.07</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>0.09</td>
<td>0.16</td>
<td>0.21</td>
<td>0.18</td>
<td>0.14</td>
<td>0.09</td>
<td>0.06</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>3.02</td>
</tr>
<tr>
<td>8</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.42</td>
<td>0.37</td>
<td>0.16</td>
<td>0.04</td>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>0.31</td>
<td>0.33</td>
<td>0.20</td>
<td>0.10</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.32</td>
</tr>
<tr>
<td>9</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.63</td>
<td>0.30</td>
<td>0.06</td>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>0.53</td>
<td>0.32</td>
<td>0.11</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.63</td>
</tr>
<tr>
<td>10</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.75</td>
<td>0.22</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>11</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.73</td>
<td>0.24</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>12</td>
<td>C₉H₁₂</td>
<td>Bz</td>
<td>0.75</td>
<td>0.23</td>
<td>0.02</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
</tr>
</tbody>
</table>

1 T = 598 K.

2 C₉H₁₂ was analyzed for three pulses only, i.e., 7th, 8th, and 9th.
TABLE IV
Isotopic Tracer Results. Injection of C\textsubscript{6}D\textsubscript{6}. T = 578 K.

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>(\phi) (atoms exch.)\textsubscript{molecule}</th>
<th>(\Sigma \times 10^{-19})</th>
<th>(1/\Sigma \times 10^{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>2.51</td>
<td>3.158</td>
<td>3.166</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>2.10</td>
<td>5.801</td>
<td>1.724</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>1.67</td>
<td>7.902</td>
<td>1.265</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.47</td>
<td>9.752</td>
<td>1.025</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>1.24</td>
<td>11.312</td>
<td>0.884</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>1.02</td>
<td>12.596</td>
<td>0.794</td>
</tr>
</tbody>
</table>

\[
1/\Sigma_{\infty} = 0.3136 \times 10^{-20} \; ; \; \Sigma_{\infty} = 3.1887 \times 10^{20}
\]

TABLE V
Isotopic Tracer Results. Injection of C\textsubscript{6}D\textsubscript{6}. T = 598 K.

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>(\phi) (atoms exch.)\textsubscript{molecule}</th>
<th>(\Sigma \times 10^{-19})</th>
<th>(1/\Sigma \times 10^{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>2.70</td>
<td>3.397</td>
<td>2.943</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>2.21</td>
<td>6.178</td>
<td>1.619</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>1.65</td>
<td>8.254</td>
<td>1.211</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.30</td>
<td>9.890</td>
<td>1.011</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>1.00</td>
<td>11.149</td>
<td>0.897</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.82</td>
<td>12.180</td>
<td>0.821</td>
</tr>
</tbody>
</table>

\[
1/\Sigma_{\infty} = 0.3745 \times 10^{-20} \; ; \; \Sigma_{\infty} = 2.6703 \times 10^{20}
\]
### TABLE VI

Isotopic Tracer Results. Injection of C₆D₆. \( T = 628 \) K.

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>( \phi (\text{atoms exch.}) ) molecule</th>
<th>( \Sigma \times 10^{-19} )</th>
<th>( 1/\Sigma \times 10^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>2.86</td>
<td>3.599</td>
<td>2.779</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.92</td>
<td>6.015</td>
<td>1.663</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>1.40</td>
<td>7.776</td>
<td>1.286</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.20</td>
<td>9.286</td>
<td>1.077</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>1.03</td>
<td>10.582</td>
<td>0.945</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.91</td>
<td>11.727</td>
<td>0.853</td>
</tr>
</tbody>
</table>

\[
1/\Sigma_\infty = 0.4968 \times 10^{-20}; \quad \Sigma_\infty = 2.0130 \times 10^{20}
\]

### TABLE VII

Isotopic Tracer Results. Injection of C₆D₆. \( T = 653 \) K.

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>( \phi (\text{atoms exch.}) ) molecule</th>
<th>( \Sigma \times 10^{-19} )</th>
<th>( 1/\Sigma \times 10^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>3.32</td>
<td>4.178</td>
<td>2.394</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>2.40</td>
<td>7.197</td>
<td>1.389</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>1.67</td>
<td>9.300</td>
<td>1.075</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.20</td>
<td>10.809</td>
<td>0.925</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.92</td>
<td>11.966</td>
<td>0.836</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.73</td>
<td>12.885</td>
<td>0.776</td>
</tr>
</tbody>
</table>

\[
1/\Sigma_\infty = 0.4383 \times 10^{-20}; \quad \Sigma_\infty = 2.2818 \times 10^{20}
\]
### TABLE VIII

Isotopic Tracer Results. Injection of \( \text{C}_9\text{H}_{12} \). \( T = 578 \text{ K.} \)

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>( \phi ) (\text{atoms exch.}) _molecule</th>
<th>( \Sigma \times 10^{-19} )</th>
<th>( 1/\Sigma \times 10^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>1.09</td>
<td>1.883</td>
<td>5.311</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.59</td>
<td>2.902</td>
<td>3.446</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>0.31</td>
<td>3.438</td>
<td>2.909</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.22</td>
<td>3.818</td>
<td>2.620</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.15</td>
<td>4.077</td>
<td>2.453</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.11</td>
<td>4.267</td>
<td>2.344</td>
</tr>
</tbody>
</table>

\( 1/\Sigma_\infty = 1.7270 \times 10^{-20} \); \( \Sigma_\infty = 0.5791 \times 10^{20} \)

### TABLE IX

Isotopic Tracer Results. Injection of \( \text{C}_9\text{H}_{12} \). \( T = 598 \text{ K.} \)

<table>
<thead>
<tr>
<th>PN</th>
<th>1/PN</th>
<th>( \phi ) (\text{atoms exch.}) _molecule</th>
<th>( \Sigma \times 10^{-19} )</th>
<th>( 1/\Sigma \times 10^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>1.80</td>
<td>3.109</td>
<td>3.216</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.85</td>
<td>4.578</td>
<td>2.185</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>0.43</td>
<td>5.320</td>
<td>1.880</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.28</td>
<td>5.804</td>
<td>1.723</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.30</td>
<td>6.322</td>
<td>1.582</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.27</td>
<td>6.789</td>
<td>1.473</td>
</tr>
</tbody>
</table>

\( 1/\Sigma_\infty = 1.1751 \times 10^{-20} \); \( \Sigma_\infty = 0.8510 \times 10^{20} \)
### TABLE X

Isotopic Tracer Results. Injection of $C_9H_{12}$. $T = 628 \, \text{K}$.

<table>
<thead>
<tr>
<th>PN</th>
<th>$1/\text{PN}$</th>
<th>$\phi_{\text{atoms exch.}}$/molecule</th>
<th>$\Sigma \times 10^{-19}$</th>
<th>$1/\Sigma \times 10^{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>2.88</td>
<td>4.975</td>
<td>2.010</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.28</td>
<td>7.186</td>
<td>1.392</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>0.79</td>
<td>8.551</td>
<td>1.170</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.46</td>
<td>9.345</td>
<td>1.070</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.35</td>
<td>9.950</td>
<td>1.005</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.23</td>
<td>10.347</td>
<td>0.966</td>
</tr>
</tbody>
</table>

\[ 1/\Sigma_\infty = 0.7558 \times 10^{-20} ; \quad \Sigma_\infty = 1.3232 \times 10^{20} \]

### TABLE XI

Isotopic Tracer Results. Injection of $C_9H_{12}$. $T = 653 \, \text{K}$.

<table>
<thead>
<tr>
<th>PN</th>
<th>$1/\text{PN}$</th>
<th>$\phi_{\text{atoms exch.}}$/molecule</th>
<th>$\Sigma \times 10^{-19}$</th>
<th>$1/\Sigma \times 10^{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>1.75</td>
<td>3.023</td>
<td>3.308</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.29</td>
<td>5.251</td>
<td>1.904</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>0.76</td>
<td>6.564</td>
<td>1.523</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.53</td>
<td>7.480</td>
<td>1.337</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.25</td>
<td>7.911</td>
<td>1.264</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.58</td>
<td>8.913</td>
<td>1.122</td>
</tr>
</tbody>
</table>

\[ 1/\Sigma_\infty = 0.6856 \times 10^{-20} ; \quad \Sigma_\infty = 1.4585 \times 10^{20} \]
Figure 18. Average number of atoms exchanged per molecule during successive passage of pulses of C₆D₆ and cumene at 578 °K.

Figure 19. Cumulative number of H atoms exchanged between the catalyst and the hydrocarbon during passage of pulses of C₆D₆ and cumene at 578 °K.
Figure 20. Average number of atoms exchanged per molecule during successive passage of pulses of C₆D₆ and cumene at 598 °K.

Figure 21. Cumulative number of H atoms exchanged between the catalyst and the hydrocarbon during passage of pulses of C₆D₆ and cumene at 598 °K.
Figure 22. Average number of atoms exchanged per molecule during successive passage of pulses of \( C_6D_6 \) and cumene at 628 °K.

Figure 23. Cumulative number of H atoms exchanged between the catalyst and the hydrocarbon during passage of pulses of \( C_6D_6 \) and cumene at 628 °K.
Figure 25. Cumulative number of H atoms exchanged between the catalyst and the hydrocarbon during passage of pulses of $\text{C}_6\text{H}_6$ and cumene at 653 K.

Figure 24. Average number of atoms exchanged per molecule passage of pulses of $\text{C}_6\text{H}_6$ and cumene at 653 K.
Figure 26. Plot of the reciprocal of the cumulative number of H atoms exchanged between the catalyst and the hydrocarbon after passage of pulses of \( \text{C}_6\text{D}_6 \) over the silica-alumina catalyst.
Figure 27. Plot of the reciprocal of the cumulative number of H atoms exchanged between the catalyst and the hydrocarbon after passage of pulses of C_{9}H_{12} over the silica-alumina catalyst.
ocal of the cumulative number of atoms exchanged at infinite number of pulses, we can assert that this number is essentially independent of the temperature at which the exchange occurs. So, the mean value of Σ is

$$\Sigma = 2.54 \pm 0.50 \times 10^{20} \text{ atoms exchanged}$$

The value determined for the most probable error came from statistical considerations only, but we feel it has little practical significance. What we consider of importance is the order of magnitude of the variable. The values of Σ obtained from the exchange during dealkylation of cumene over the partially deuterated catalyst are in all instances smaller than the average value of Σ obtained from C₆D₆. This is what we expected since not all the original H atoms on the catalyst had been exchanged after passage of the six pulses of C₆D₆.

If we now make use of the average value of Σ as the number of H atoms on this catalyst sample, we can determine the concentration of H atoms on the surface of the catalyst. Using the value of the surface area of half a gram of catalyst, we have

$$\frac{\text{H atoms}}{\text{cm}^2} = \frac{\Sigma}{0.5 \text{ S.A. (cm}^2\text{)}} = 1.8 \times 10^{14} \frac{\text{H atoms}}{\text{cm}^2}$$

Furthermore, the area per H atom is

$$\frac{\text{area}}{\text{H atom}} = 54.76 \frac{A^2}{\text{H atom}}$$

Finally we can calculate the turnover frequency, T.F., i.e., the number of molecules cracked per H atom per second initially, at the various temperatures used for the dealkylation reaction. These values will be given by
where \( \frac{dX}{dt} \) is the initial rate of reaction, at the beginning of the catalyst bed, and equal to the pseudohomogeneous rate constant by virtue of Equation \(-19\):

\[
\frac{dX}{dt} = k(1-X) \quad \text{or} \quad \frac{dX}{dt} |_{X=0} = k
\]

\( n_0 \) in Equation \(-49\) is the initial number of cumene molecules injected and is equal to \( 8.6369 \times 10^8 \). \( E_\infty \) is the mean value of H atoms on the surface of this catalyst sample (half a gram).

Thus,

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>( k_{\text{homo}} )</th>
<th>T.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>578</td>
<td>0.4221</td>
<td>0.0145</td>
</tr>
<tr>
<td>598</td>
<td>0.6548</td>
<td>0.0223</td>
</tr>
<tr>
<td>628</td>
<td>1.2004</td>
<td>0.0408</td>
</tr>
<tr>
<td>653</td>
<td>1.9064</td>
<td>0.0648</td>
</tr>
</tbody>
</table>

Earlier in the text we mentioned our assumption that cumene suffered the same type of exchange as benzene did, namely, rapid exchange or scrambling until statistical equilibrium. However, in the cumene molecule two general classes of hydrogen atoms are present: ring hydrogen atoms and chain (alkyl) hydrogen atoms. Thus, we might expect a certain difference in the exchange rates of these two groups of hydrogen atoms with the deuterium atoms at the surface of catalyst.

Figure 28a shows the fragmentation pattern of a blank sample of
Figure 28. Mass spectra of (a) cumene blank and (b) cumene (unreacted) passed over the deuterated catalyst, PN 7. Ionizing voltage: 10 v.
cumene at a nominal ionizing voltage of 10 volts. This pattern reflects the main features of the fragmentation patterns reported in API Research Project 44 at ionizing voltages of 50 and 75 volts. The differences between them are the shifting of the base peak from 120 m/e (parent peak) for the low voltage pattern to 105 m/e for the high voltage one and the absence of ring cleavage at low ionizing voltage. Our experimental spectrum was started at an accelerating voltage of 1200 volts (m/e = 30).

Figures 28b and 29a,b show the fragmentation patterns of samples of unreacted cumene after passage of three successive pulses of C_{9}H_{12} over a partially deuterated catalyst. It is clear from these patterns that the exchange occurred to an extensive degree. At least 11 peaks (before correction due to natural occurrence of ^{13}C) are observable in the m/e region from 120 m/e to 131 m/e, i.e., C_{9}H_{12-i}D_{i} species, i = 0,1,2,...,12. Also, exchange of hydrogen atoms in number exceeding the ring H atoms is observed for the C_{9} species (105 m/e). The benzene species portion is seen here because some traces of product benzene were unavoidably collected in the sample tubes as was some CO_{2} from air.

In spite of the extensive degree of the exchange of the cumene molecule, the deuterium distribution does not satisfy exactly a statistical binomial distribution because of the different rates of exchange of the ring hydrogen atoms (faster exchange) and chain hydrogen atoms. Even more, there are differences among the hydrogen chain atoms as well as among the ring atoms.

In the C_{3} portion of the patterns (40 m/e), peaks corresponding to masses (m/e ratios) higher than 43 (with exception of m/e = 44 mainly
Figure 29. Mass spectra of cumene (unreacted) passed over the deuterated catalyst (a) PN 8 and (b) PN 9. Ionizing voltage: 10 v.
due to CO₂) were not observed indicating that the degree of exchange in the C₃ part of the cumene molecule did not occur extensively.

Figures 30 and 31 show the deuterium distribution in cumene and in benzene, respectively, and how they are compared with the binomial distribution after the passage of the 7th and 8th pulses over a deuterated catalyst. We can observe that the individual fittings are good. However, if we look at hydrogen:deuterium ratio (H/D) for each compound in these two pulses we note a certain difference.

\[
\begin{align*}
\text{PN 7} & \quad (H/D)_{BZ} = 2.33 & (H/D)_{Cu} = 2.97 \\
\text{PN 8} & \quad (H/D)_{BZ} = 6.06 & (H/D)_{Cu} = 8.09
\end{align*}
\]

The difference between the H/D ratios for successive pulse becomes greater. This fact can be explained arguing that as we increase the pulse number, the amount of deuterium available from the surface decreases and consequently the cumene molecule is disfavored during the exchange.

RADIOACTIVE TRACER EXPERIMENTS

Tracer experiments with radioactive ¹⁴C were carried out to examine the reversibility of the overall dealkylation reaction. At the same time these tracer experiments allowed us to determine thermodynamic properties of this process.

The results of the radioactive tracer experiments using a mixture of benzene-¹⁴C and cumene are shown in Figures 32 and 33. The activity per unit area in a total time of 40 minutes for products benzene and cumene is shown as a function of the percent conversion (% conv) of cumene to products. The activity was calculated from the number of counts in the LSC (corrected by subtracting from the gross count of a
Figure 30. Deuterium distribution in cumene after passage of the seventh and eighth pulses of $\text{C}_9\text{H}_{12}$ over the silica-alumina catalyst at 598 °K. Solid lines: experimental. Dashed lines: theoretical binomial distribution.
Figure 31. Deuterium distribution in benzene after passage of the seventh and eighth pulses of C_6H_12 over the silica-alumina catalyst at 598 °K. Solid lines: experimental. Dashed lines: theoretical binomial distribution.
Figure 32. Activity of benzene and cumene after passage of a mixture of benzene$^{14}$C: cumene over the silica-alumina catalyst at (a) 325 °C and (b) 350 °C.
Figure 33. Activity of benzene and cumene after passage of a mixture of benzene-14C:cumene over the silica-alumina catalyst at (a) 375 °C and (b) 400 °C.
sample the value corresponding to a blank sample) divided by the appropriate chromatographic area. The values of the percent conversion used in these figures take into account the initial amount of benzene present (as benzene-\textsuperscript{14}C), mainly 21%.

The activity for benzene decreases as percent conversion increases, due to the dilution effect that occurred as more benzene was produced by the reaction. The activity for benzene, in all cases, shows a trend to a stabilized value, presumably the equilibrium value, that is dependent on the Bz-\textsuperscript{14}C:Cu ratio in the starting mixture at the given temperature. What is important to consider is the fact that the activity of cumene maintains a zero or almost zero value until the conversion becomes high indicating that the reverse reaction (alkylation) does not occur to any considerable extent.

Experimentally, it was very difficult to achieve degrees of conversion greater than those shown in the figures, as we increased the contact time of the reactant with the catalyst. This observation suggested that the reaction was essentially at equilibrium. Figures 34 and 35 show plots of % conversion against the contact time \(\tau(W/Q_o)\) where the conversion percentage has been corrected by subtracting the initial "percent of conversion", i.e., the amount of benzene initially present was subtracted for each sample. They show that at each temperature an "equilibrium" value of conversion was almost achieved.

Bearing in mind that we can calculate the equilibrium conversion at any temperature (provided we know the cumene partial pressure) and hence some thermodynamic properties of this process, we made use of the mathematical formulation given in Appendix II to achieve these goals. There,
Figure 34. Percent of conversion of cumene to products as a function of the contact time $t/W$ at (a) 325°C and (b) 350°C.
Figure 35. Percent of conversion of cumene to products as a function of the contact time (W/G) at (a) 375 °C and (b) 400 °C.
we postulate a model of a reversible reaction of first order and neglect any change in volume. The results are shown in Figure 36 where the reciprocal of fractional conversion is plotted against the reciprocal of contact time. The intercepts are the values of reciprocal equilibrium conversions for each temperature. The fitting of the data to a straight line is quite satisfactory.

Considering now the equilibrium reaction

\[ C_{9\text{H}_{12}} \rightleftharpoons C_{6\text{H}_{6}} + C_{3\text{H}_{6}} \]

we can express the equilibrium constant as

\[ K_p = \frac{P_{C_{6\text{H}_{6}}} P_{C_{3\text{H}_{6}}}}{P_{C_{9\text{H}_{12}}}} \]

or in terms of fractional conversion at equilibrium

\[ K = \frac{x_e^2}{(1-x_e)} \left( P_{C_{9\text{H}_{12}}} \right)_0 \]

and

\[ P_{C_{9\text{H}_{12}}} = \left( P_{C_{9\text{H}_{12}}} \right)_0 (1-x_e) \]

\[ P_{C_{3\text{H}_{6}}} = P_{C_{6\text{H}_{6}}} = \left( P_{C_{9\text{H}_{12}}} \right)_0 x_e \]

If we assume stoichiometric formation of \( C_{6\text{H}_{6}} \) and \( C_{3\text{H}_{6}} \), as indicated by the chemical reaction, the above equations result.

In Table II we tabulated the theoretical values of the equilibrium conversion for the dealkylation of cumene as function of initial pressure of cumene and temperature. So, by using the experimental value ob-
Figure 36. Reciprocal of the fractional conversion of cumene to products versus the reciprocal of the contact time.
tained for the equilibrium conversion at a given temperature we can
determine at what initial pressure of cumene we are performing this re-
action. Using the experimental data given in Appendix II at \( T = 350^\circ C \),
for example, \( (\text{conv})_\text{eq} = 0.8131 \) and from Table II this corresponds to
\[ P_{\text{C}_9\text{H}_{12}} = 0.05 \text{ atm (38 mm Hg)} \]. Appendix II also tabulates the results
for the equilibrium constants at each temperature using the expressions
given above.

The standard Gibbs free energy \( \Delta G^o \) can be calculated from
\[
\Delta G^o = -RT \ln K_{eq}
\]

Using the temperature coefficient of the equilibrium constant, given
by the vant Hoff's expression
\[
\frac{d\ln K}{dT} = \frac{\Delta H^o}{RT^2}
\]
and assuming \( \Delta H^o \) is constant over the range of temperature studied, this
property can also be determined. Figure 37 shows the results of a plot
of \( \ln K_{eq} \) versus \( 1/T \).

Finally, we can obtain the value of the standard entropy of the re-
action from
\[
\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}
\]

Table XII summarizes the value of all these properties. The values
are in good agreement with the theoretical values calculated from stand-
ard properties of formation of the individual compounds participating in
the reaction. The value of \( \Delta H^o \) is somewhat lower than the theoretical
one (17.54 kcal mole\(^{-1}\) compared with 22-23 kcal mole\(^{-1}\)) but we must re-
call the assumption made of independence of \( \Delta H^o \) with temperature and
Figure 37. Plot for the determination of the standard enthalpy of reaction, $\Delta H^\circ$. 
TABLE XII

Thermodynamic Properties for the Equilibrium Reaction\(^1\)

\[
\ce{C_6H_5 C_3H_7 \leftrightarrow C_6H_6 + C_3H_6}
\]

<table>
<thead>
<tr>
<th>T, °C</th>
<th>(X_{eq})</th>
<th>(K_{eq}, \text{atm})</th>
<th>(\ln K_{eq})</th>
<th>(G^\circ, \text{kcal mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>0.7282</td>
<td>(9.75 \times 10^{-2})</td>
<td>-2.3274</td>
<td>2.77</td>
</tr>
<tr>
<td>350</td>
<td>0.8131</td>
<td>(1.77 \times 10^{-1})</td>
<td>-1.7323</td>
<td>2.14</td>
</tr>
<tr>
<td>375</td>
<td>0.8745</td>
<td>(3.05 \times 10^{-1})</td>
<td>-1.1885</td>
<td>1.53</td>
</tr>
<tr>
<td>400</td>
<td>0.8744</td>
<td>(3.04 \times 10^{-1})</td>
<td>-1.1895</td>
<td>1.59</td>
</tr>
</tbody>
</table>

\(\Delta H^\circ = 17.54 \text{ kcal mole}^{-1}; \ \Delta S^\circ = 24.71 \text{ cal mole}^{-1}\text{degree}^{-1}\).

\(^1\) All thermodynamic properties have been calculated on the assumption that the gases behave ideally.
also the fact that experimentally we have, occurring simultaneously with the cracking process, reactions that may affect this value, e.g., coke formation, isomerizations, alkylation, etc. The values of the thermodynamic properties for the 400°C do not agree with the theoretical values. We suspect that diffusion phenomena might have influenced these results and we will consider it in the discussion.
IV. DISCUSSION

In this thesis work we have presented results of experiments regarding the deactivation of a silica-alumina catalyst during the dealkylation of cumene; kinetic parameters based upon the assumption of a first order behavior with respect to reactant cumene; deuterium isotope tracer studies; and the reversibility of the dealkylation reaction by means of radioactive tracer compounds.

Based upon these results and the review of the literature discussed in Section I, we would like to outline certain ideas and schemes concerning the cracking of iso-propyl benzene on silica-alumina catalysts. We will also discuss here the nature of the active sites responsible for the catalyst activity and criticize some of the traditional assumptions about the mechanism of this classical test reaction for acid cracking catalysts.

The discussion will be divided into several parts. The first one will be concerned with the deactivation or aging of the catalyst and the kinetics of the reaction. The second and third parts will deal with the results and implications of the deuterium tracer studies and the nature of the active sites. The fourth part will involve a discussion about the reversibility of the cumene cracking reaction in view of the radioactive tracer results and thermodynamic considerations. Finally, we will discuss a probable mechanism for this reaction in light of all the considerations mentioned above.

DEACTIVATION OF THE CATALYST AND KINETICS

We have found that in this pulse system the decay of the catalyst follows an empirical first order equation with respect to the initial
activity, that is, the initial fractional conversion, \( X \), of cumene to products, viz,

\[- \frac{dX}{d(PN)} = k X \tag{56}\]

This initial activity is a function of the temperature, as seen in Figure 6, and we can assume that it is a function of the fraction of surface sites that remains unpoisoned as well. This equation does not appear to hold over the entire range, for it would predict zero conversion at infinite pulse number. In contrast, the data tend to "line out" or stabilize at a fairly constant conversion, \( X_e \), which is a function of temperature. Furthermore, it predicts that \( k \) is not a function of temperature. Integration of the equation given above with boundary conditions \( X = X_1 \) at \( PN = 1 \), yields an equation that allows the calculation of \( k \), the constant of the deactivation process.

\[
\ln X = \ln X_1 - k(PN-1) \tag{57}\]

Of course, \( X \) varies with temperature. Assuming an Arrhenius type dependence on the temperature for \( k \), we can then obtain an activation energy for the deactivation process by determining \( k \) at various \( X_1 \)'s, or at various \( T \)'s, even though \( k \) was assumed to be independent of \( T \). Thus, \( k \) has the value

\[
k = 1.44 \times 10^{-2} \exp \left( \frac{1.339.5}{RT} \right) ;
\]

where the \( E_{\text{act}} \) is

\[
E_{\text{act}} = -1.34 \text{ kcal mole}^{-1} .
\]

This value of \(-1.34 \text{ kcal/mole}\) is indeed near zero, as the empirical Equation \(-13\) predicts. The small positive slope (or negative acti-
vation energy) in the Arrhenius expression indicates that deactivation is faster at lower temperatures, i.e., the steady state with respect to deactivation is reached faster at lower temperatures. It should be again stressed that the activation energy reported for this process is quite small. Now, in order to give an explanation to these results, we will first discuss what was found by Wojciechoski's work (13-20,42).

Testing Wojciechoski's model (13,42) of catalyst decay as a function of time-on-stream, Campbell and Wojciechoski (15) and Best and Wojciechoski (16,20) found experimentally that the catalyst they used (La-Y zeolite) showed a deactivation pattern that allowed its classification as a catalyst Class II or $N = 1$ ($N$ is one of the aging parameters of Wojciechoski's theory, as defined by Equation -11- in this work). If the normally accepted assumption by Corrigan (10-12) that the cracking reaction of cumene occurs on a single site, then $m$, the number of active sites lost in the deactivation event, should be equal to 2. In (15,16,20) it was argued that a value of $m = 2$ indicates that the deactivation occurs by a Hinshelwood mechanism in which two sites are lost in every deactivation event, or it proceeds by adsorption of a poison on two sites. An analysis (15,16,20) of the other aging parameter $G$ (also defined in Equation -11-) shows that it behaves in a similar way to the $k$, defined in our case, that is, it decreases as temperature increases. However, $G$ contains two terms that are dependent on the temperature, and if the rate constant for deactivation is to behave in a typical manner to the rate constants ($k_d$ should increase when increasing $T$), the other temperature dependent term, $[P]$, concentration of poison, must have a larger exponential term, such that
\[ k_d = \text{const} \frac{G}{[P]} = \text{const'} \exp\left(\frac{E_P}{RT}\right) \]

and \((g-p) < 0\).

If \([P]\) is given by an expression derived by assuming a two-site Hinshelwood mechanism and knowing (49) that the heats of adsorption of propylene, benzene, and cumene increase in this order, then cumene has to be the poisoning agent and not any of the reaction products, benzene or propylene.

In view of their similar behavior, we can draw a parallel between our observed deactivation rate constant \(k\) and Wojciechoski's aging parameter \(G\). Furthermore, we can arrive to the same conclusions provided that our catalyst belongs to Class II \((N = 1)\) according to Wojciechoski's theory. So, making the assumption of single site adsorption of the reactant, \(m\), the number of active sites lost per deactivating event is equal to 2, and the decay should take place by a mechanism like the one described above with cumene being the poisoning agent. There is still a possibility, as suggested by Pratter and Lago (11), that the deactivation process might be the consequence of impurities in the reactant cumene. As mentioned earlier (see page 42) our analysis did not reveal the presence of such impurities; moreover, the results of our experiments with different "kinds" of cumene show that the decay is still present in the case of purified cumene. These results argue against an impurity as the source of deactivation.

Another interesting result from our study on the decay of catalyst is the one regarding the stabilization of the catalyst at degree of conversion approximately equal to two-thirds the initial conversion at all
temperatures. This suggests that the same fraction of surface sites has been deactivated. Voorhies (43) in a study on the cracking of an East Texas Gas Oil on a fresh silica-alumina catalyst, observed that the deposited carbon on the catalyst, after a given period of time and at a given temperature, was relatively independent of the feed rate of the gas oil, hexadecane, or decalin. This means that when a given feed is cracked at different flow rates at a given temperature and process period, the coke on the catalyst is relatively constant. This fact in turn would mean that significant kinetic results could be derived once this stage or "plateau" has been achieved.

Knowing that significant results can be obtained from a stabilized catalyst, we have reported Arrhenius parameters in agreement with a first order kinetics scheme with respect to reactant cumene. The pulse technique using a microcatalytic reactor presents some inconveniences when the determination of kinetic parameters is concerned (44). These inconveniences arise because of the uncertainties involved in knowing the actual partial pressures of reactants and products, which change continuously through the bed; it must also be added that adsorption on the catalyst is not a simple process. The contact time is not known with certainty since the initial pulse is distorted because the bed acts as a small chromatographic column. However, this fact can be used to propose a mechanism for the surface reaction if we accept that it is the rate limiting step in the cracking process, i.e., diffusion phenomena are not controlling and adsorption and desorption equilibria are quickly reached.

Thus, a Langmuir-Hinshelwood mechanism can explain our kinetic re-
sults, assuming single site adsorption for the reactant cumene in agreement with the literature (10-12,14-16,20) and weakly adsorbed products. So, the rate is given by

\[
\text{rate} = k_2 \theta_{\text{Cu}} = \frac{k_2 K_{\text{Cu}} P_{\text{Cu}}}{1 + K_{\text{Cu}} P_{\text{Cu}}}
\]

Having a dispersion phenomenon of the reactant through the catalyst bed, as we have described, we can safely say that the reactant pressure will be low and the degree of coverage of the surface small, simplifying the expression to

\[
\text{rate} = k_{\text{obs}} P_{\text{Cu}} = k_2 K_{\text{Cu}} P_{\text{Cu}}
\]

where the observed rate constant is the product of the true rate constant times the adsorption equilibrium constant of cumene. Using the Arrhenius expression

\[
\frac{3 \ln k_{\text{obs}}}{3T} = \frac{3 \ln k_2}{3T} + \frac{3 \ln K_{\text{Cu}}}{3T}
\]

or in terms of energies

\[
E_{\text{obs}} = E_{\text{true}} - \lambda_{\text{Cu}}
\]

where \(\lambda_{\text{Cu}}\) is the heat of adsorption of cumene. Therefore, the true activation energy for the cracking reaction would be the addition of the observed activation energy plus the heat of adsorption of cumene.

Pansing and Malloy (45) have reported a value of \(\lambda_{\text{Cu}}\) equal to 6.4 kcal/mole which added to our observed activation energy gives as a result for the true activation energy \(E_{\text{true}} = 21.4\) kcal mole\(^{-1}\). This value is in good agreement with values reported in the literature (12,14,
on similar catalysts. A mechanism as the one proposed here is similar to mechanisms proposed by Pratter and Lago (11) and Wojciechoski and co-workers (14,16,20).

In this work we have reported that benzene and propylene are not the only products of the cracking reaction. Small, but detectable, amounts of ethyl benzene have been reported as well as the Arrhenius parameters when this product is considered in the calculation of the fractional conversion of cumene to products. In (18) it was reported the presence of at least 60 products in the cumene cracking reaction. The implications of the presence of ethyl benzene among the reaction products will be discussed in greater detail when we deal with the nature of the active centers on the catalyst.

DEUTERIUM TRACER RESULTS

One of the first conclusions that can be reached from the results of the experiments with deuterium tracers is that the H-D exchange is very fast and that it approaches statistical scrambling. It is known (38) that this exchange occurs at temperatures below the temperatures required for the cracking, which gives support to the hypothesis that the H (or D) atoms are removed or added to the hydrocarbon with great facility. This is required in a carbonium ion or radical mechanism and suggests that the rate limiting step for the process should not be the cleavage of the C-H bond. Also, by the use of stable isotopes it has been noted that what appeared to be a relatively simple heterogeneous catalytic reaction involves, in fact, a complicated mechanism. All C-H and catalyst-H bonds appear to be very labile under the reaction conditions.
The mathematical derivation given in Appendix I supplies the tools needed for the calculation of the number of H atoms that can be exchanged (H atoms on the surface). We obtained a value of $\Gamma_\infty = 2.54 \times 10^{20}$ per 0.5 gm of catalyst, and this number was used to calculate the number of H atoms per area of catalyst, viz

$$1.8 \times 10^{14} \, \frac{\text{H atoms}}{\text{cm}^2} \quad \text{or} \quad 1.8 \times 10^{18} \, \frac{\text{H atoms}}{\text{m}^2}$$

This number compares favorably with values of number of active sites reported in the literature. It is larger than the number of sites per m² given by Pratter and Lago (11) and Horton and Maatman (12) for similar catalysts. We must say, however, that the number of sites reported by these authors, derived from the absolute rate theory, is dependent on the reaction temperature (see Equation -6- of this work) whereas in our case we have that the number of active sites is independent on the reaction temperature (see Fig. 26). We do believe, however, that the H atom concentration must be a function of the pretreatment temperature as suggested by Hall et al. (24). On the other hand, the number of active sites is smaller than the one reported by Best and Wojciechoski (16) for a La-Y zeolite which seems obvious since this latter catalyst is a more active one. One last point in reference to the works of Pratter and Lago (11) and Horton and Maatman (12) is that these authors used silica-alumina catalysts with lower percentages of aluminum, 10% Al (11) and impregnated catalysts of low Al content and a cogelled catalyst (10% Al) (12). It can be argued that a lower content of Al means a lower concentration of hydroxyl groups on the surface of the catalyst, which in turn means a lower number of H atoms available for exchange. Besides, since
B₀ (number of active sites according to these authors) is a function of the temperature, B₀ is then a measure of the number of centers used during reaction at a given temperature, whereas Σ∞ counts all the sites (Brønsted) susceptible of participation in the cracking if this process is to use these centers (Brønsted sites). Therefore, Σ∞ would be an upper limit to the number of active sites. This effect can be noted in Figure 27 which indicates that the cracking reaction used a smaller number of centers and also the Σ∞ values obtained therein are dependent on the temperature.

Our study on the relative distribution of deuterium in cumene shows that the exchange occurs very rapidly and in number (per molecule) that exceeds the number of ring H atoms. This relative distribution can be fit to a statistical binomial distribution, but however, the H-D exchange in the ring portion of the molecule is faster (or larger for a given period of time) than the exchange in the chain giving weight to a carbinium ion mechanism. This fact was also observed by Galeski (29) on a silica-magnesia catalyst; he noted that the propylene initially obtained was not exchanged.

NATURE OF THE ACTIVE SITES

As we mentioned in the Introduction section, a carbinium ion mechanism is the commonly accepted mechanism to explain the catalytic cracking of iso-propyl benzene. Our stable isotope studies also agree with this.

Two mechanisms for the formation of carbinium ions are generally accepted (38,46)

a. Donation of a proton to a double bond

\[ \text{H}^+ (\text{Brønsted site}) \quad \text{C} \quad \text{C} \quad \text{H}^+ \]

\[ \text{C} \quad \text{C} \quad \text{H}^+ \]
b. Abstraction of a hydride from a saturated hydrocarbon molecule

\[
\begin{array}{c}
\text{\large \text{C} \text{C} - \text{H}} \\
\text{\large \text{\text{-H}}} \\
\text{\large (Lewis site)} \\
\text{\large \text{C} \text{C}}
\end{array}
\]

As we mentioned in the Introduction, it has been established that if the ring exchange is faster (or bigger for a given period) than chain exchange, a carbonium ion mechanism due to the addition of a proton to a double bond in the ring is favored. Considerations with respect to the stabilization by resonance of the carbonium ion so formed give support to this model,

\text{I} \quad \text{II} \quad \text{III}

The same argument (resonance) has been given to support the anti-Markonikov’s addition as suggested by Thomas (9).

In view of the elevated number of Brønsted sites as evidenced by the stable isotope experiments, it is safe to think, in principle, that these Brønsted sites are the responsible centers for the catalytic activity in the cracking of cumene. Best and Wojciechoski (18) in their exhaustive study on the identification of the primary and secondary products of this reaction arrived at the same conclusion. Even more, the unquestionable presence of Lewis active sites is referred to by these authors as being responsible for the production of some secondary products, such as is the case of ethylbenzene. It is easy for us now to
give an adequate explanation to the formation in small quantities of this compound and to its higher activation energy as evidenced by Figure 13. In (18) experiments were conducted where the temperature of regeneration of the catalyst was increased (Lewis acid sites increase and Brønsted acid sites remain constant before decreasing), and it was found that the selectivity of those compounds suspected to be formed by a mechanism using Lewis acid sites increased. Conversely, the selectivity of those initiated by a protonic addition decreased.

The suggested mechanism for the formation of the reaction products are then

1. Formation of benzene and propylene

2. Formation of ethyl benzene
In the second step of the mechanism for the formation of ethyl benzene, the nucleophilic attack of the benzene ring must take place before a migration of a hydride occurs on the alkyl group, in which case di-iso-propyl benzene would be produced (it is unlikely that di-iso-propyl benzene is formed this way as the resultant ion would be a phenonium ion). In the last step the elimination of a proton produces styrene, but this product is thermodynamically unfavored (18) and the addition of a hydride ion from the adsorption site seems more probable. We mention again that our analysis never showed the presence of a compound such as cymene.

REVERSIBILITY OF THE DEALKYLATION REACTION

It appears that the interpretation of the results of the studies of reversibility of the cumene cracking reaction by means of radioactive tracers is straightforward. The results shown in Figures 32 and 33 give support to the hypothesis that the reaction occurs reversibly when high temperatures and low pressures are used. The thermodynamic analysis based upon a model of reversible first order reactions at equilibrium agrees reasonably with the theory. The difference between the value of the heat of reaction reported here and the enthalpy of reaction calculated from the heats of formation of the compounds can be explained by taking into account the presence of parallel or secondary reactions together with the cracking. Data taken close to equilibrium are in good agreement with our model. For the calculation of \( K_{eq} \) we made use of an approximate value of the initial pressure of cumene corresponding to 0.05 atm. If the initial dispersion of the reactant pulse is considered to be Gaussian (44) or rectangular top (47,48), the low value of the initial pressure is acceptable. Also, this initial pulse distribution
would give support to our assumption that the density of the system did not change in the derivation of the first order kinetics since the high value of the ratio \( \frac{P_{\text{He}}}{P_{\text{Cu}}} \) for each pulse at total pressure \( P_{\text{t}} = 167 \text{ atm.} \)

Finally, it is worth pointing out that from studies with radioactive isotopes it is possible to obtain the rate constant for the forward reaction, since the slope of the plot \( 1/X \) versus \( 1/t \) is equal to \( 1/k_1 \) (see Appendix II); and these results also compare favorably with the results obtained from the kinetic studies. For example, at \( 325^\circ \text{C} \), \( k_1 = 0.3188 \text{ sec}^{-1} \) from the radioactive isotope experiment at that temperature and at \( 325^\circ \text{C} \)

\[
k = 0.77 \times 10^5 \exp(-\frac{7.436.3}{598}) \quad \text{Equation -26-}
\]

\[
k = 0.3061 \text{ sec}^{-1}
\]

In Figure 36 the behavior of \( 1/X \) versus \( 1/t \) at \( 400^\circ \text{C} \) is not what was expected, since both the slope and intercept were out of line with values obtained at lower temperatures. This is likely due to kinetic disguise brought about by the onset of diffusional control at the fast rate observed at the higher temperature.

**REACTION MECHANISM**

Two main reaction mechanistic schemes have been principally used to explain the dealkylation reaction: Pratter and Lago (11) and Wojciechowski and collaborators (14-16,18,20). The difference between these two mechanisms is the adsorption of all the compounds on the surface assumed in the \( \Delta \) mechanism of Campbell and Wojciechowski (14). Our findings are in agreement with these two schemes in a general manner, but certain
discrepancies exist with respect to the deactivation of the catalyst in our case and the deactivation of the catalyst as suggested by Pratter and Lago (11). On the other hand, we have evidence that the reaction takes place irreversibly at small space times (at high temperatures and low pressures).

Thus the mechanistic scheme of reaction proposed here is

\[
\begin{align*}
C + S & \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} CS \overset{k_2}{\rightarrow} P + BS \\
& \overset{k_{-3}}{\underset{k_3}{\rightarrow}} B + S
\end{align*}
\]

\[
C + 2S \overset{k_4}{\underset{k_{-4}}{\rightleftharpoons}} CS_2 \text{ (coke)}
\]

where C, B, P, and S represent cumene, benzene, propylene, and surface sites, respectively.

The dealkylation reaction takes place by a Langmuir-Hinshelwood mechanism having as the rate limiting step the cleavage of a C-C bond (rapid H-D exchange) eliminates the breaking of C-H bonds as the limiting step). The desorption of the products should be fast.

So,

\[
\text{rate} = k_2 \theta_{Cu} = \frac{k_2 K_{Cu} p_{Cu}}{(1 + K_{Cu} p_{Cu} + K_{Bz} p_{Bz} + K_{Pr} p_{Pr})}
\]

The deactivation reaction follows a process of the Hinshelwood type where two sites are eliminated in each deactivating event or the poison adsorbs on two sites.

\[
\text{rate (deact.)} = k_4 \theta^2 - k_{-4} (1-\theta)^2
\]
V. SUMMARY

In the study of the catalytic cracking of iso-propyl benzene over a silica-alumina catalyst, Houdry M-46, in a microcatalytic reactor using the pulse technique, we obtained the following results:

1. The catalyst suffers a period of initial deactivation. This initial deactivation was found to be first order with respect to the initial activity.

2. The deactivation pattern of this catalyst allowed us to propose a Hinshelwood mechanism where two active sites are lost per deactivating event or adsorption of the poison occurs on two sites. We found that cumene is the precursor of the poisoning.

3. We found no conclusive evidence that impurities in the reactant cumene could be responsible for the deactivation of the catalyst.

4. The dealkylation reaction follows first order kinetics with respect to reactant cumene with a true activation energy being $E_{\text{true}} = 21.4$ kcal mole$^{-1}$.

5. The reaction occurs irreversibly at high temperatures and low pressures.

6. The mechanism of reaction involves the formation of carbonium ions by the addition of a proton from a Brønsted acid site on the surface of the catalyst to the ring portion of the molecule.

7. The presence of Lewis acid sites can explain the formation of secondary products.

8. The kinetic scheme for the dealkylation reaction is expressed by a Langmuir-Hinshelwood mechanism where the adsorption of reactant is on a single site and the adsorption of products is negligible.
9. An upper limit for the number of active sites (Brønsted) has been set by means of H-D exchange experiments, namely, $1.8 \times 10^{18}$ sites/m$^2$.

10. The H-D exchange experiments demonstrated that the hydrocarbon C-H bonds as well as the catalyst-H bonds are very labile, and exchange occurs to statistical scrambling at the temperatures used for the cracking. This fact indicates that the C-H bond cleavage is not the rate limiting step and eliminates the possibility of a kinetic isotope effect from this source.
VI. REFERENCES


APPENDIX I

Prediction of the Total Number of Deuterium Atoms Exchanged as a Function of the Pulse Number (37).

Consider the isothermal H-D exchange reaction of a hydrocarbon with a catalyst surface. Let us assume that at a time interval equal to the contact time $N_{HC}$ molecules of the hydrocarbon are allowed to achieve equilibrium with the catalyst. Four different types of interactions between the hydrocarbon molecules and the surface can be described:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H \leftrightarrow D$</td>
</tr>
<tr>
<td>2</td>
<td>$H \leftrightarrow H$</td>
</tr>
<tr>
<td>3</td>
<td>$D \leftrightarrow D$</td>
</tr>
<tr>
<td>4</td>
<td>$D \leftrightarrow H$</td>
</tr>
</tbody>
</table>

Let us assume that these interactions are proportional to the number of the relevant species on the surface and in the gas phase, i.e., the molecules cannot distinguish between H and D atoms. We note that interactions of the types 2 and 3 produce no net change in the molecule nor in the surface whereas in the steady state the rates of the interactions 1 and 4 must be equal. Thus, if we denote

- $\theta$ as the number of D atoms per hydrocarbon molecule,
- $(n-\theta)$ as the number of H atoms per hydrocarbon molecule,
- $N$ as the total number of interactions or exchanges, and
- $F$ as the fraction of deuterated surface and knowing that the rate of H exchange should be equal to the rate of D exchange, we have

\[ F = \frac{N - \theta}{n - \theta} \]
\[ r_H = N(n - \theta)F \]
\[ r_D = N\theta(1 - F) \]
\[ r_H = r_D \]
\[ (n - \theta)F = \theta(1 - F) \]
\[ \theta = nF \]  

(1)

Now, let us define

\[ D_s = \text{number of D atoms on the surface} \]
\[ D_g = \text{number of D atoms in the gas phase} \]
\[ \Sigma_\infty = \text{total number of sites on the surface available for H-D exchange} \]

In view of these definitions, we have

\[ D_g = N_{HC}\phi \]  
\[ F = D_s/\Sigma_\infty \]  

(2)

(3)

Now substituting (2) and (3) into (1) we obtain

\[ N_{HC}\theta = nN_{HC}D_s/\Sigma_\infty = D_g \]  

(4)

So far we have assumed that a hydrocarbon molecule or pulse has been allowed to interact with the catalyst surface and to attain equilibrium. This pulse will be swept away and a new one will be added. For each new pulse we have \( nN_{HC} \) deuterium atoms injected. The mass balance equation for a given pulse is given by

\[ D_g^i + D_s^i = nN_{HC} + D_s^{i-1} \]  

(5)

where the superscripts refer to pulse number.
Thus, substituting (4) in (5) and defining \( \theta = \frac{nN_{HC}}{\Sigma_{\infty}} \)

\[
\frac{D_j^j}{s} = \frac{\theta \Sigma_{\infty} + D_{j-1}}{(1 + \theta)}
\]

Let us suppose that initially a certain amount of deuterium is present on the surface of the catalyst and that it is given by

\[
D_0^s = s \theta \Sigma_{\infty} \quad (s = 0, \text{ for a deuterium free surface}).
\]

Then, the amount of deuterium on the surface after each new pulse added is

\[
\frac{1}{D_s} = \frac{\theta \Sigma_{\infty} + s \theta \Sigma_{\infty}}{(1 + \theta)} = \frac{\theta \Sigma_{\infty} (1 + s)}{(1 + \theta)}
\]

\[
D_1^s = \frac{\theta \Sigma_{\infty} + \left[ \frac{\theta \Sigma(1+s)}{(1+\theta)} \right]}{(1 + \theta)} = \frac{\theta \Sigma_{\infty} \left[ (1+\theta) + 1 + s \right]}{(1 + \theta)^2}
\]

\[
D_2^s = \frac{\theta \Sigma_{\infty} [(1+\theta)^2 + (1+\theta) + 1 + s]}{(1 + \theta)^3}
\]

By induction

\[
D_n^s = \frac{\theta \Sigma_{\infty}}{(1 + \theta)^n} \left[ s + \sum_{i=0}^{PN-1} \theta^i \right]
\]

\[
\text{The term } \sum_{i=0}^{PN-1} (1 + \theta)^i \text{ represents the sum of the } n \text{ terms of a geometric progression of common ratio } r = (1 + \theta) \text{ with first term } a_1 = 1 \text{ and nth term } a_n = (1 + \theta)^{PN-1}. \text{ For such geometric progression the sum of the } n \text{ terms is given by}
\]

\[
S_n = a_1 \frac{1 - r^n}{1 - r} = \frac{1 - (1 + \theta)^{PN}}{1 - (1 + \theta)}
\]
Therefore,

\[
\begin{align*}
D_s^{PN} &= \frac{\Theta E_\infty}{(1+\Theta)^{PN}} \left[ s + \frac{1 - (1+\Theta)^{PN}}{1 - (1+\Theta)} \right] \\
D_s^{0} &= \Sigma + D_s^{0} \\
\Sigma &= D_s^{PN} - D_s^{0} \\
\Sigma &= \frac{\theta E_\infty}{(1+\Theta)^{PN}} \left[ s + \frac{1 - (1+\Theta)^{PN}}{1 - (1+\Theta)} \right] - s \Theta E_\infty \\
\end{align*}
\]

after some algebraic manipulation

\[
\begin{align*}
\frac{1}{\Sigma} &= \frac{\frac{1}{\Sigma_\infty}}{\Sigma_\infty} \left[ \frac{\left[ 1 - (1+\Theta)^{PN} \right] - 1}{(1-s\Theta) \left[ 1 - (1+\Theta)^{PN} \right]} \right] \\
\frac{1}{\Sigma} &= \frac{\frac{1}{\Sigma_\infty}}{\Sigma_\infty^2} \left[ \frac{1}{(1-s\Theta)} - \frac{1}{(1-s\Theta) \left[ 1 - (1+\Theta)^{PN} \right]} \right] \\
\end{align*}
\]

now, expanding \((1 + \Theta)^{PN}\) into a Taylor's series, according to

\[
a^x = 1 + \ln a + (\ln a)^2/2! + (\ln a)^3/3! + ... \]

\[
\frac{1}{\Sigma} = \frac{1}{\Sigma_\infty} \left[ \frac{\left( 1 - (1+\Theta)^{PN} \right) - 1}{(1-s\Theta) \left[ 1 - (1+\Theta)^{PN} \right]} \right] \\
\frac{1}{\Sigma} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{(1-s\Theta)} - \frac{1}{1 - [1+PN\ln(1+\Theta) + \frac{(PN\ln(1+\Theta))^2}{2!} + ...]} \right] \\
\]

if \(PN\) and \(\Theta\) are small we can neglect 2nd and higher order terms, so
\[ \frac{1}{\Sigma} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{(1-s\theta)} + \frac{1}{(1-s\theta)\ln(1+\theta)} - \frac{1}{PN} \right] \]

Thus we have that a plot of $1/\Sigma$ versus $1/PN$ should be a straight
line with intercept and slope equal to

\[
\text{intercept} = \frac{1}{\Sigma_\infty} \left\{ \frac{1}{(1-s\theta)} \right\}
\]

\[
\text{slope} = \frac{1}{\Sigma_\infty} \left\{ \frac{1}{(1-s\theta)\ln(1+\theta)} \right\}
\]

We note that if we start with a deuterium free surface, $s = 0$, the
intercept reduces to $1/\Sigma_\infty$, i.e., the reciprocal of the total number of
sites available for H-D exchange.
Consider the reaction
\[
\begin{array}{cccc}
\text{A} & \xrightarrow{k_1} & \text{Prod} \\
& \text{and assume it to be a) a reversible first order reaction and b) the volume is kept constant. Its rate will be given by the expression}
\end{array}
\]
\[
\frac{dC_{\text{Prod}}}{dt} = - \frac{dC_A}{dt} = C_{A_0} \frac{dX}{dt} = k_1 C_A - k_2 C_{\text{Prod}}
\]
\[
= k_1 (C_{A_0} - X C_{A_0}) - k_2 C_{A_0} X
\]
\[
= C_{A_0} (k_1 (1 - X) - k_2 X)
\]
where \(C_{A_0}\) is the initial concentration of reactant A and \(X\) is the fractional conversion.
At equilibrium \(\frac{dC_A}{dt} = 0\) and \(k_1 (1 - X_e) = k_2 X_e\)
\[
\frac{k_1}{k_2} = K_c = \frac{X_e}{(1 - X_e)} ; \quad K_c = K = \text{equilibrium constant.}
\]
Now, plugging this expression into the rate equation
\[
\frac{dX}{dt} = k_1 (1 - X) - k_2 X_e \frac{(1 - X_e)}{X_e} X
\]
after rearrangement
\[
\frac{dX}{dt} = k_1 \left( \frac{X_e - X}{X_e} \right)
\]
integration of which yields

$$\ln \left( \frac{X_e - X}{X_e} \right) = -\frac{k_1 t}{X_e} \quad \text{or} \quad X = X_e \left( 1 + \frac{1}{\exp \left( \frac{k_1 t}{X_e} \right)} \right)$$

Expanding $\exp \left( \frac{k_1 t}{X_e} \right)$ into a series according to

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \quad ; \quad x = \frac{k_1 t}{X_e} \quad 1$$

and neglecting terms of second and higher orders, we have

$$X = X_e \left( 1 + \frac{1}{k_1 t} \right)$$

which, after algebraic manipulation, is reduced to

$$X = \frac{X_e k_1 t}{X_e + k_1 t}$$

or in linear form

$$\frac{1}{X} = \frac{1}{X_e} + \frac{1}{k_1 t}$$

Thus a plot of $1/X$, reciprocal of the fractional conversion, versus $1/t$, the reciprocal of the contact time, should be a straight line with intercept equal to $1/X_e$ and slope equal to $1/k_1$.

If we now return to the cumene cracking reaction and assume it follows the model outlined above with the equilibrium constant given by Equation -52-

$$K_p = \frac{x_e^2}{1 - X_e} P_c$$
we can obtain values of this equilibrium constant from the intercept of 
the plot of \(1/X_e\) versus \(1/t\) and a partial pressure of cumene as 
described in the text. Once the equilibrium constant has been calculated 
for every temperature we can make use of the vant Hoff's expression

\[
\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}
\]

to obtain the enthalpy of the reaction \(H^0\) by plotting \(\ln K\) versus \(1/T\) as 
in Figure 37.

**DATA USED IN AND RESULTS OBTAINED FROM FIGURES 32 TO 37**

\[T = 325^\circ C = 598\; K\]

<table>
<thead>
<tr>
<th>% Conv (+ Bz-(^{14})C)</th>
<th>Conv (-Bz-(^{14})C)</th>
<th>1/Conv</th>
<th>T(W/Q)</th>
<th>1/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.15</td>
<td>0.0000</td>
<td>----</td>
<td>0.00</td>
<td>----</td>
</tr>
<tr>
<td>38.81</td>
<td>0.1766</td>
<td>5.6625</td>
<td>0.72</td>
<td>1.3889</td>
</tr>
<tr>
<td>42.57</td>
<td>0.2142</td>
<td>4.6685</td>
<td>1.00</td>
<td>1.0000</td>
</tr>
<tr>
<td>52.21</td>
<td>0.3106</td>
<td>3.2196</td>
<td>1.60</td>
<td>0.6250</td>
</tr>
<tr>
<td>54.92</td>
<td>0.3377</td>
<td>2.9612</td>
<td>2.00</td>
<td>0.5000</td>
</tr>
<tr>
<td>61.54</td>
<td>0.4039</td>
<td>2.4759</td>
<td>3.00</td>
<td>0.3333</td>
</tr>
<tr>
<td>70.78</td>
<td>0.4963</td>
<td>2.0149</td>
<td>4.00</td>
<td>0.2500</td>
</tr>
<tr>
<td>71.41</td>
<td>0.5026</td>
<td>1.9897</td>
<td>5.00</td>
<td>0.2000</td>
</tr>
<tr>
<td>71.21</td>
<td>0.5006</td>
<td>1.9976</td>
<td>6.00</td>
<td>0.1667</td>
</tr>
</tbody>
</table>

\[X_e = 0.7282\; ;\; k_1 = 0.3188\; ;\; K_{eq} = 9.75 \times 10^{-2} \; atm.\]

\[T = 350^\circ C = 623\; K\]

<table>
<thead>
<tr>
<th>% Conv (+ Bz-(^{14})C)</th>
<th>Conv (-Bz-(^{14})C)</th>
<th>1/Conv</th>
<th>T(W/Q)</th>
<th>1/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.15</td>
<td>0.0000</td>
<td>----</td>
<td>0.00</td>
<td>----</td>
</tr>
<tr>
<td>56.50</td>
<td>0.3535</td>
<td>2.8289</td>
<td>1.00</td>
<td>1.0000</td>
</tr>
</tbody>
</table>
\[ X_e = 0.8131 \; ; \; k_1 = 0.6528 \; ; \; K_{eq} = 1.77 \times 10^{-1} \text{ atm.} \]

\[ T = 375^\circ \text{C} = 648 \text{ K} \]

<table>
<thead>
<tr>
<th>% Conv ((+\text{Bz}^{-14}\text{C}))</th>
<th>Conv ((-\text{Bz}^{-14}\text{C}))</th>
<th>(1/\text{Conv})</th>
<th>(T(W/Q))</th>
<th>(1/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.74</td>
<td>0.3959</td>
<td>2.5259</td>
<td>1.20</td>
<td>0.8333</td>
</tr>
<tr>
<td>70.56</td>
<td>0.4941</td>
<td>2.0239</td>
<td>1.60</td>
<td>0.6250</td>
</tr>
<tr>
<td>71.69</td>
<td>0.5054</td>
<td>1.9786</td>
<td>2.00</td>
<td>0.5000</td>
</tr>
<tr>
<td>76.13</td>
<td>0.5498</td>
<td>1.8188</td>
<td>2.40</td>
<td>0.4167</td>
</tr>
<tr>
<td>78.00</td>
<td>0.5368</td>
<td>1.8629</td>
<td>2.60</td>
<td>0.3846</td>
</tr>
<tr>
<td>76.12</td>
<td>0.5497</td>
<td>1.8192</td>
<td>2.80</td>
<td>0.3571</td>
</tr>
<tr>
<td>78.00</td>
<td>0.5685</td>
<td>1.7590</td>
<td>3.00</td>
<td>0.3333</td>
</tr>
<tr>
<td>81.71</td>
<td>0.6056</td>
<td>1.6513</td>
<td>4.00</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

\[ X_e = 0.8745 \; ; \; k_1 = 1.1840 \; ; \; K_{eq} = 3.05 \times 10^{-1} \text{ atm.} \]

\[ T = 400^\circ \text{C} = 673 \text{ K} \]

<table>
<thead>
<tr>
<th>% Conv ((+\text{Bz}^{-14}\text{C}))</th>
<th>Conv ((-\text{Bz}^{-14}\text{C}))</th>
<th>(1/\text{Conv})</th>
<th>(T(W/Q))</th>
<th>(1/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.15</td>
<td>0.0000</td>
<td>----</td>
<td>0.00</td>
<td>----</td>
</tr>
<tr>
<td>70.25</td>
<td>0.4910</td>
<td>2.0367</td>
<td>1.00</td>
<td>1.0000</td>
</tr>
<tr>
<td>75.63</td>
<td>0.5448</td>
<td>1.8355</td>
<td>1.20</td>
<td>0.8333</td>
</tr>
<tr>
<td>83.55</td>
<td>0.6240</td>
<td>1.6026</td>
<td>1.60</td>
<td>0.6250</td>
</tr>
<tr>
<td>88.32</td>
<td>0.6717</td>
<td>1.4888</td>
<td>2.40</td>
<td>0.4167</td>
</tr>
<tr>
<td>91.58</td>
<td>0.7043</td>
<td>1.4198</td>
<td>2.80</td>
<td>0.3571</td>
</tr>
<tr>
<td>91.65</td>
<td>0.7050</td>
<td>1.4184</td>
<td>4.00</td>
<td>0.2500</td>
</tr>
<tr>
<td>% Conv (+Bz-^14C)</td>
<td>Conv (-Bz-^14C)</td>
<td>1/Conv</td>
<td>T(W/Q)</td>
<td>1/T</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
<td>-----</td>
</tr>
<tr>
<td>76.16</td>
<td>0.5501</td>
<td>1.8179</td>
<td>1.00</td>
<td>1.0000</td>
</tr>
<tr>
<td>82.63</td>
<td>0.6148</td>
<td>1.6265</td>
<td>1.60</td>
<td>0.6250</td>
</tr>
<tr>
<td>88.38</td>
<td>0.6723</td>
<td>1.4874</td>
<td>2.00</td>
<td>0.5000</td>
</tr>
<tr>
<td>92.61</td>
<td>0.7146</td>
<td>1.3994</td>
<td>3.00</td>
<td>0.3333</td>
</tr>
<tr>
<td>94.45</td>
<td>0.7330</td>
<td>1.3643</td>
<td>4.00</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

\[ X_e = 0.8744 \; ; \; k_1 = 1.3223 \; ; \; K_{eq} = 3.04 \times 10^{-1} \text{ atm.} \]

LINEAR FITTING FOR THE \( \Delta H^0 \) DETERMINATION

<table>
<thead>
<tr>
<th>( \frac{-\ln K_{eq}}{1/T \times 10^3, ^\circ K^{-1}} )</th>
<th>( 1/T \times 10^3, ^\circ K^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3274</td>
<td>1.6722</td>
</tr>
<tr>
<td>1.7323</td>
<td>1.6051</td>
</tr>
<tr>
<td>1.1885</td>
<td>1.5432</td>
</tr>
</tbody>
</table>

Intercept: 12.435
Slope: -8,827.2

Correlation coefficient, \( r^2 = -0.999996 \)
APPENDIX III

Determinition of Initial Slope in Deactivation

Plot in Figure 5

A. Approximation Method

<table>
<thead>
<tr>
<th>T, °C</th>
<th>-dX/dPN</th>
<th>ln(-dX/dPN)</th>
<th>X₀</th>
<th>ln X₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>0.00900</td>
<td>-4.7105</td>
<td>0.165</td>
<td>-1.802</td>
</tr>
<tr>
<td>275</td>
<td>0.01700</td>
<td>-4.0745</td>
<td>0.325</td>
<td>-1.124</td>
</tr>
<tr>
<td>303</td>
<td>0.02650</td>
<td>-3.6306</td>
<td>0.405</td>
<td>-0.904</td>
</tr>
<tr>
<td>349</td>
<td>0.02620</td>
<td>-3.6420</td>
<td>0.475</td>
<td>-0.744</td>
</tr>
</tbody>
</table>

Linear regression fitting:

Intercept: -2.7879
Slope: 1.07263
r²: 0.9832

B. Limiting Secant Method

<table>
<thead>
<tr>
<th>T, °C</th>
<th>-dX/dPN</th>
<th>ln(-dX/dPN)</th>
<th>X₀</th>
<th>ln X₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>0.01125</td>
<td>-4.4874</td>
<td>0.165</td>
<td>-1.802</td>
</tr>
<tr>
<td>275</td>
<td>0.01896</td>
<td>-3.9660</td>
<td>0.325</td>
<td>-1.124</td>
</tr>
<tr>
<td>303</td>
<td>0.02500</td>
<td>-3.6889</td>
<td>0.405</td>
<td>-0.904</td>
</tr>
<tr>
<td>349</td>
<td>0.02600</td>
<td>-3.6497</td>
<td>0.475</td>
<td>-0.744</td>
</tr>
</tbody>
</table>

Linear regression fitting:

Intercept: -3.0058
Slope: 0.82389
r²: 0.99338

Average slope: n = 0.94826; standard deviation = 0.1759
Order of Decay, n = 0.95 ± 0.18